Western States Petroleum Association
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Kevin Buchan
Manager, Bay Area Region

February 16, 2017

Chair Marcus, and Members of the Board
State Water Resources Control Board
1001 I Street
Sacramento, CA 95812-2000

via e-mail at: commentletters@waterboards.ca.gov

Re: WSPA Comments on Beneficial Uses and Mercury Objectives

Dear Chair Marcus and Members of the Board:

The Western States Petroleum Association (WSPA) is a non-profit trade association representing companies that explore for, produce, refine, transport and market petroleum, petroleum products, natural gas and other energy supplies in California and four other western states. WSPA offers this comment package with attachments on the State Water Resources Control Board's (Board's) proposed "Part 2 of the Water Quality Control Plan for Inland Surface Waters, Enclosed Bays, and Estuaries of California – Tribal and Subsistence Fishing Beneficial Uses and Mercury Provisions" (Mercury Provisions), which was released for public review on January 3, 2017.

Attached are our detailed technical and legal comments, along with the supporting referenced documents. Due to the large size of the attachments, we are emailing our comments in multiple submittal components.

Executive Summary

While stakeholders were aware that the State Water Board was considering these new Draft Provisions, along with the voluminous supporting documents (over 700 pages of information and technical documents), they were not made available to the public for review and comment until January 3, 2017. This has left the regulated public with only 45 days to review, evaluate, and comment on the extensive Draft Provisions.

WSPA reiterates our request for an extension to the comment period.

WSPA is concerned that the State Water Board has combined issues in the Draft Provisions that are only superficially related. While WSPA understands the Board's desire to assist the U.S. EPA in meeting its June 30, 2017 Consent Decree deadline for adopting mercury objectives relating to wildlife, this deadline does not require that the Board rush to adopt the other portions of the Draft Provisions.

WSPA requests the Board implement a phased approach whereby the wildlife-related objectives are implemented in time to meet the June 30, 2017 Consent Decree deadline.

It is not clear from the Draft Staff Report or Draft Provisions that reasonable achievability of the objectives, or a program for implementation, has been sufficiently considered by the Board, or will be

considered by the Regional Water Boards before designating the new beneficial uses and associated water quality objectives.

WSPA requests that more attention and focus be given to reasonable achievability and implementation of the objectives prior to designation of any water bodies, and that such achievability analysis and implementation program be specifically required in accordance with the Water Code §§ 13050 and 13241(c).

In addition to requiring reasonable achievability of objectives and an implementation program, the Water Code also requires the Board to take into account "economic considerations" when setting water quality objectives. (Water Code § 13241(d)). This has not been adequately completed in the Draft Staff Report.

WSPA is concerned that the Draft Provisions do not require the Regional Water Boards to conduct a use attainability analysis prior to designating water bodies with the new T-SUB, SUB, or CUL beneficial uses. This is in conflict with the federal Clean Water Act (CWA), 40 C.F.R. § 131.10(j)(1), which requires states to conduct a use attainability analysis as described in 40 C.F.R. § 131.10(g) whenever designating uses not specified in section 101(a)(2) of the CWA.

WSPA is concerned that the Draft Provisions do not give appropriate guidance to the Regional Water Boards tasked with implementing and assigning the three new beneficial uses to water bodies in their regions. WSPA urges the Board to adopt clear guidance that the Regional Water Boards must follow when considering evidence regarding water bodies being considered for these new beneficial use designations.

The Substitute Environmental Document (SED) portion of the Draft Staff Report purports to analyze the environmental impacts resulting from reasonably foreseeable means of compliance, as required by the California Environmental Quality Act (CEQA). Even in a programmatic review of a regulatory action that is intended to benefit the environment, CEQA requires a full and fair evaluation of its potential to result in adverse environmental side-effects. The SED refers vaguely to "major facility upgrades" and "additional infrastructure" that will be needed for at least some number of publicly owned and industrial wastewater treatment facilities to comply with effluent limitations that will result from the new objectives Without adequately evaluating the environmental impacts of treatment facility upgrades, the SED fails to fulfill the basic requirements for a CEQA document.

The proposed effluent limitations for individual NPDES dischargers may not be attainable (especially 1 ng/L).

Consistent with Board precedent, dilution credits and mixing zones should be allowed, if warranted by site-specific conditions, for NPDES discharges containing mercury.

Unless significant changes are made to the Draft Provisions, the State Board should also implement a variance policy because, in many cases, the proposed water quality objectives will be unattainable.

Mercury concentrations in many of the state's water bodies have exceeded the proposed objectives for decades or longer. As such, certain beneficial uses are not existing uses as defined by the Clean Water Act. The proposed Draft Provisions should be modified to provide guidance regarding implementation measures and time schedules for "goal uses."

The proposed fish tissue objectives for the protection of human health and wildlife are likely too conservative, and the proposed water column targets are flawed. Neither the objectives nor the targets should be adopted at this time.

The implementation program in the State's proposed policy should be modified to focus on implementation actions that will lead to reductions in mercury in the state's waters and fish.

WSPA appreciates the opportunity to submit our comments, and looks forward to reviewing Staff's responses. Thank you.

Sincerely,

Kevin Buchan

Enclosures:

Pillsbury Memorandum, "Comment Letter, Beneficial Uses and Mercury Objectives"

Exponent External Memorandum, "Technical Comments on the State Board's Mercury Provisions"

Referenced Materials in Support of WSPA Comment letter, pdf

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MEMORANDUM

To: Kevin Buchan
Western States Petroleum Association

From: Margaret Rosegay, Norman Carlin, Stella Pulman

Date: February 16, 2017

Re: Comment Letter - Beneficial Uses and Mercury Objectives

Pillsbury prepared these comments on behalf of the Western States Petroleum Association (WSPA) regarding the Proposed Part 2 of the Water Quality Control Plan for Inland Surface Waters, Enclosed Bays, and Estuaries of California – Tribal and Subsistence Fishing Beneficial Uses and Mercury Provisions, dated January 3, 2017 (hereinafter referred to as the "Draft Provisions" or "Draft Staff Report").

I. Process and timeline for adoption

A. Failure to give adequate time to review/provide meaningful comments on lengthy and complex Draft Provisions

While stakeholders were aware that the State Water Board was considering these new Draft Provisions, in part to assist the U.S. EPA in complying with its Consent Decree requirements by the June 30, 2017 deadline, the Draft Provisions themselves, along with the voluminous supporting documents (over 700 pages of information and technical documents), were not made available to the public for review and comment until January 3, 2017. This has left the regulated public with only 45 days to review, evaluate, and comment on the extensive, and at times complex, Draft Provisions. Such a short comment window does not provide a reasonable opportunity for comment or input by the public and therefore WSPA reiterates its request for an extension of the comment period.

B. Wildlife criteria should be implemented and considered separately from other Draft Provisions.

WSPA is concerned that the State Water Board has combined issues in the Draft Provisions that are only superficially related. While WSPA understands the Board's desire to

assist the U.S. EPA in meeting its June 30, 2017 Consent Decree deadline for adopting mercury objectives relating to wildlife, this deadline does not require that the Board rush to adopt the other portions of the Draft Provisions, namely the three new categories of beneficial uses (T-SUB, SUB, and CUL) and associated objectives. Instead, the Board should implement a phased approach whereby the wildlife-related objectives are implemented in time to meet the June 30, 2017 Consent Decree deadline, while the remainder of the Draft Provisions can be set out on a different track to allow the regulated community a chance to fully consider and understand the technical and scientific implications of the issues.

II. Inadequate notice

A. Draft Provisions will have far broader impacts on dischargers than identified by the Board

In reviewing the Draft Provisions and Draft Staff Report, WSPA notes that the full implications of the Draft Provisions are not identified or addressed by the Board. This failure to fully brief the issues, and be transparent about all of the implications of this proposed regulatory action, deprives the public of adequate notice.

The Draft Provisions and Draft Staff Report focus on new mercury objectives that are designed to protect human health and wildlife. These objectives are expressed in mercury fish tissue levels. However, the other key element of the Draft Provisions is the development of three new beneficial uses, two of which are based on subsistence fishing (T-SUB and SUB). The Board briefly acknowledges in the Draft Staff Report that attaining water quality sufficient to support these two subsistence fishing uses is not dependent on mercury alone. "Another complication is that the attainability of a subsistence objective would depend on the levels of other contaminants in the fish tissue, not just mercury." (Draft Staff Report p. 113) For example, there are other bioaccumulative contaminants present in state water bodies, such as PCBs, selenium, and dieldrin, which must be at acceptable levels in fish tissue before the subsistence uses can actually be supported. As stated in the Draft Staff Report: "[A]lthough the issue here is limited to evaluating whether the beneficial uses should be established and defined, designating and protecting these uses will come with challenges. There are a few contaminants, including mercury and PCBs, which accumulate in fish tissue and can prevent many water bodies from supporting a subsistence level of fish consumption in California." (Draft Staff Report, p. 106)

Therefore, WSPA is concerned that this action, while clearly flagging the mercury issue for the regulated public, fails to put stakeholders on notice that *other* permit effluent limits and/or TMDLs may be reopened in order to achieve the beneficial uses described in the Draft Provisions. This means that other interested parties may not have an opportunity to comment on these Draft Provisions since the full spectrum of impacts are not discussed in the Draft Staff Report or even identified in the notice.

III. Arbitrary and capricious to target permitted point source dischargers when objectives will not be achieved through such targeting; economics not properly considered

A. Focusing mercury reductions on municipal and industrial dischargers will not achieve the state's objectives given the small relative contribution of these sources

While WSPA is sympathetic to the environmental justice implications involved in creating the new beneficial uses and the public health goals behind setting ambitious objectives with respect to mercury concentrations in fish tissue, WSPA is concerned that the Draft Provisions will not and cannot achieve the stated objectives associated with the new beneficial uses.

As recognized in the Draft Staff Report, mercury is a contaminant that accumulates in fish tissue and persists in the environment such that, "[e]ven if all sources of the contaminants are eliminated, the contaminants are likely to remain high for decades. . . . Further, current sources may not be directly regulated by water boards (e.g. atmospheric emissions, naturally occurring in soils, or geothermal sources)." (Draft Staff Report, p. 106).

Water Code § 13050 requires water quality control plans to include "a program for implementation needed for achieving water quality objectives." In addition, prior to setting water quality objectives, the Water Code requires the State Water Board to consider the "[w]ater quality conditions that could reasonably be achieved through the coordinated control of all factors which affect water quality in the area." (Water Code § 13241(c)) The State Water Board has itself made statements indicating doubts about the achievability of the water quality objectives associated with the new subsistence beneficial uses. In the Draft Staff Report, the Board states, "[o]nly a fraction of waters would be able to currently support fish that meet a subsistence-type water quality objective when applied to TL4 fish. In fact, many waters do not have fish that would meet the water quality objective for recreational fishers," and the objectives for subsistence uses are roughly "three to four times more stringent than the objective to protect recreational fishing." (Draft Staff Report p 113). Further, the Board notes that attainability of a subsistence objective "would depend on the levels of other contaminants in the fish tissue, not just mercury," and some waters have elevated levels of other contaminants like dieldrin and PCBs "which may prevent attainment of a subsistence-type objective *even if* mercury concentrations are low enough." (Draft Staff Report p 113, emphasis added).

As exemplified throughout the Draft Staff Report (*e.g.*, Table N-11), watershed contributions of mercury vary significantly depending upon source type. In fact, the largest contributors of mercury are not permitted sources such as municipal wastewater and

industrial dischargers with NPDES permits. Rather, the largest mercury sources are tributaries, sediment deposition from non-point sources, and legacy mining operations.

While WSPA recognizes that mercury objectives are important to protect beneficial uses, the stringency and focus of control in order to achieve those objectives should be commensurate with the source and its corresponding mercury loading. Tighter controls for NPDES point sources will not result in significant reductions in mercury levels to achieve the state's objectives. Instead, the state should focus more effort, investment, and resources on controlling discharges from non-point sources such as legacy mining sites.

It is not clear from the Draft Staff Report or Draft Provisions that reasonable achievability of the objectives, or a program for implementation, has been sufficiently considered by the Board, or will be considered by the Regional Water Boards before designating the new beneficial uses and associated water quality objectives. WSPA requests that more attention and focus be given to reasonable achievability and implementation of the objectives prior to designation of any water bodies, and that such achievability analysis and implementation program be specifically required in accordance with the Water Code §§ 13050 and 13241(c).

B. The Board has failed to adequately consider economic factors when setting the objectives

In addition to requiring reasonable achievability of objectives and an implementation program, the Water Code also requires the Board to take into account "economic considerations" when setting water quality objectives. (Water Code § 13241(d)). This has not been adequately completed in the Draft Staff Report.

While the Draft Staff Report purports to include the required economic factors analysis in Appendix R, Appendix R entirely omits the most essential portion of the analysis. When discussing the facility upgrades that will be necessary in order to meet the 1 ng/l objective, Appendix R states, "WWTPs that need reductions to meet limits corresponding to lower values, such as those derived from the tribal subsistence objective (1 ng/L) may not be able to do so with tertiary treatment. Due to the limited information on the permittees likely to be subject to this target, *this analysis does not estimate costs for complying with the 1 ng/L target.*" (Draft Staff Report, Appendix R, p R-46 (emphasis added); *see also* p R-50). Moreover, while the Draft Staff Report assumes, without evidence, that the 4 ng/L limitation is achievable with tertiary treatment, data from the Central Valley Regional Board (discussed in WSPA's accompanying technical comments) indicate that tertiary treatment cannot achieve the 4 ng/L limit in all cases. This amounts to an admission that the economic consideration necessary to evaluate the new water quality objectives has not been done as required by the Water Code.

Therefore, the Board must complete an evaluation of economic considerations for all objectives established in the Draft Provisions.

Information on which to base the requisite economic analysis is readily available for the types of advanced treatment technologies that would be necessary to reach the 1 ng/L target. For example, a report titled "Treatment Technology Review and Assessment" prepared by the Association of Washington Businesses, Association of Washington Cities, and Washington State Association of Counties in 2013 (Treatment Technology Report, attached to these comments for incorporation in the record) evaluated advanced treatment processes, specifically membrane filtration/reverse osmosis (MF/RO) and membrane filtration/granulated activated carbon (MF/GAC). The report found that advanced treatment processes incur "significant capital and operating costs," raising the estimated capital cost of treatment from $17 to $29 dollars per gallon per day of capacity, an over 70% increases in capital costs. (Treatment Technology Report, p. ES-2). In addition, the annual operation and maintenance costs triple with the addition of advance treatment options, from approximately $5 million to $15 million. (*Id.*) Use of MF/RO increases costs from $15–$32 million in per gallon day of capacity to $28–$60 million in per gallon per day of capacity by requiring larger aeration basins, additional pumping stations, new membrane facilities, and additional energy and chemical demand. (Treatment Technology Report, p. 39). Similarly, the use of MF/GAC increases costs from $23–$50 million in per gallon per day capacity to $36–$78 million in per gallon day of capacity due to the larger aeration basins, additional pumping stations, GAC facilities, additional energy demand, GAC media replacements, and hauling and fees to regenerate GAC off-site. (Treatment Technology Report, p. 40).

IV. Impact on TMDLs

A. Contradictory information on Draft Provisions' impact on TMDLs

The Draft Staff Report and Executive Summary thereof, contain numerous representations and interpretations of the Draft Provisions' impact on TMDLs, indicating that the Draft Provisions will not apply to dischargers under TMDLs. For example, in the Executive Summary, the Board states,

> The Provisions which modify the SIP are exclusive to reasonable potential analyses and effluent limitations for mercury. ***These modifications do not apply to dischargers to waters that have site-specific mercury water quality objectives or to dischargers that discharge to receiving waters for which a mercury or methylmercury total maximum daily load (TMDL) has been approved.***

Executive Summary p. xx, emphasis added. However, other portions of the Draft Staff Report contradict the above statements by indicating that if one of the new subsistence beneficial uses (T-SUB or SUB) is assigned to a TMDL-regulated water body, the TMDL may be reopened to include the more stringent subsistence objectives. (Draft Staff Report, p. 156)

These contradictory statements, at a minimum, need clarification from the Board so the regulated public understands the potential consequences of this action. If it is in fact the intent of the Board that the Draft Provisions will not supersede a mercury TMDL (as is stated in the Executive Summary), then this needs to be stated clearly and consistently throughout the Draft Staff Report and Draft Provisions. If this is the intention of the Board, then WSPA recommends that the Board modify the Draft Provisions, Chapter IV.D.1., as follows:

> *The implementation provisions of Chapter IV.D shall be implemented through NPDES permits issued pursuant to section 402 of the Clean Water Act, water quality certifications issued pursuant to section 401 of the Clean Water Act, waste discharge requirements (WDRs), and waivers of WDRs, where any of the MERCURY WATER QUALITY OBJECTIVES apply. The implementation provisions ~~pertaining to a particular beneficial use~~ do not apply to dischargers that discharge to receiving waters for which a mercury or methylmercury total maximum daily load (TMDL) is established ~~pertaining to the same beneficial use or uses.~~*

If, instead, it is the intention of the Board to allow reopening of mercury TMDLs in order to accommodate new objectives associated with the Draft Provisions, then WSPA urges the Board to reconsider this position. The mercury TMDLs are the result of multi-year, complex processes that involved consideration of all sources of mercury to the various water body systems. These sources were evaluated for their respective contributions of mercury and the mitigation measures available to control these contributions. As noted in the San Francisco Bay TMDL, for example, the industrial and municipal wastewater point source contributions comprise only 1.5 percent of the total mercury contributions to the system. Therefore, reopening the TMDL for the purpose of amending effluent limitations for individual industrial point sources will not meaningfully affect mercury concentrations in the system to allow attainment of more stringent objectives, and instead will only serve to disrupt achievement of the long term goals of the TMDLs that are the result of years of study and negotiation.

V. Development and implementation of new beneficial uses

A. Use attainability analyses must be required prior to designation of new beneficial uses

WSPA is concerned that the Draft Provisions do not require the Regional Water Boards to conduct a use attainability analysis prior to designating water bodies with the new T-SUB, SUB, or CUL beneficial uses. This is in conflict with the federal Clean Water Act (CWA), 40 C.F.R. § 131.10(j)(1), which requires states to conduct a use attainability analysis as described in 40 C.F.R. § 131.10(g) whenever designating uses not specified in section 101(a)(2) of the CWA. The uses described in section 101(a)(2) of the CWA are colloquially known as the "fishable-swimmable" uses. The provision sets forth a national goal of attaining water quality "which provides for the protection and propagation of fish, shellfish, and wildlife and provides for recreation in and on the water . . ." 33 U.S.C. § 1251 (a)(2). The T-SUB, SUB, and CUL beneficial uses described in the Draft Staff Report and Draft Provisions fall outside of these "fishable-swimmable" uses under the CWA, and therefore a use attainability analysis must be conducted before the State can designate any water bodies as falling under these beneficial uses.

This is particularly important where, as here, the Board has recognized that the objectives associated with the new beneficial uses may be unattainable, regardless of reductions in point source mercury discharges. (*see* Draft Staff Report p. 113) Given the challenges associated with the new beneficial uses and objectives, and pursuant to CWA requirements, WSPA requests that the Board amend the Draft Provisions and Draft Staff Report to provide that use attainability analyses in accordance with 40 C.F.R. § 131.10(g) must be conducted as a prerequisite to designating any water bodies with the new beneficial uses T-SUB, SUB, and CUL.

B. Insufficient detail regarding designation of new beneficial uses by Regional Water Boards

WSPA is concerned that the Draft Provisions do not give appropriate guidance to the Regional Water Boards tasked with implementing and assigning the three new beneficial uses to water bodies in their regions. This lack of guidance may result in a great discrepancy in how the Draft Provisions are applied in the nine Regions, and could lead to different applications and designations using varying criteria. This will result in great uncertainty and potential unfairness for the regulated community.

The Draft Provisions require only one specific criterion be met before designating a water body with the new T-SUB beneficial use, which is simply that a California Native American Tribe must confirm that the designation is appropriate. (Draft Provisions, ch. II). There are no criteria built into the Draft Provisions relating to the other two new

beneficial uses (SUB and CUL), or any further criteria relating to the T-SUB use. The Draft Staff Report provides examples of information the Regional Water Boards *may* take into consideration when deciding whether to designate a particular water body, but does not require the Boards look at any or all of the example information before making a decision. (Draft Staff Report, p. 108).

WSPA is concerned that a lack of basic criteria that must be factored into every designating decision will lead to wildly different and unpredictable results across regions, as well as results that may be politically, rather than scientifically, driven. For example, while the Draft Staff Report suggests that it "may not be reasonable to designate a beneficial use . . . if only one individual is using the water in a way that would meet the beneficial use definition," the Draft Provisions do not prohibit such application. (Draft Staff Report p 109) The Draft Staff Report also recommends that community consumption studies would preferably be peer reviewed, although this also is not a requirement. (Draft Staff Report p 108)

In order to avoid vastly different applications of the Draft Provisions and ensure state-wide consistency in implementation, WSPA urges the Board to adopt clear guidance that the Regional Water Boards must follow when considering evidence regarding water bodies being considered for these new beneficial use designations.

C. Narrative objective for the SUB beneficial use is vague and subject to vast discrepancies in application across the State

WSPA is concerned that the decision to assign a narrative water quality objective to the new SUB beneficial use creates a vague and unworkable standard that cannot be applied consistently or fairly across the state. As noted in the Draft Staff Report, using a narrative objective is more flexible and can be easily tailored to a water body (Draft Staff Report p 118); however, this is precisely the downside of a narrative objective as well, since it provides no guidance or predictability for the regulated public. This problem is compounded by the fact that the Board has not imposed any guidelines or standards on the type of evidence required before a water body can be designated with the SUB beneficial use. The Board has not even required there to be a peer-reviewed consumption study conducted for the water body, which should be a bare minimum standard imposed prior to assigning what could be an extremely restrictive beneficial use and water quality objective.

The Board itself recognizes these risks, stating "[t]he disadvantage is that the objective may be interpreted in different ways, making the implementation of the objective inconsistent. . . For instance, the objective could be interpreted in eight different ways in eight different permits, resulting in eight different effluent limitations." (Draft Staff Report p. 118). WSPA urges the Board to reconsider the narrative objective for the

SUB beneficial use because the uncertainty it holds for the regulated public, as well as the risk of enormously uneven application amongst dischargers, is not an acceptable regulatory scheme.

VI. Implementation of Draft Provisions

A. Amendment of basin plans should occur before any permit changes

WSPA is concerned that the implementation of the Draft Provisions, and particularly designation of the new beneficial uses, is not being done in a way consistent with past practices of the Board or Regional Water Boards. In a typical circumstance, the Regional Water Boards would go through the public process to amend their basin plans to designate the beneficial use attributable to particular water bodies. In this way, the regulated public would be given notice that certain water quality objectives will apply based on the beneficial uses identified in the basin plan, and the public would at that time be able to comment on the designations and participate in the process of identifying and substantiating the uses.

The Draft Staff Report indicates that this orderly and typical process will not necessarily be followed with respect to the new beneficial uses. Rather, according to the Draft Staff Report, Regional Water Boards can incorporate the subsistence fishing objectives in a permit "prior to formal designation if the Water Boards determine that tribal subsistence or subsistence fishing is an existing use." (Draft Staff Report, p. 11).

This permit-by-permit approach denies the public an opportunity to comment on the designation decision, which can have significant implications for stakeholders. It also places permit holders at a distinct disadvantage and at risk of additional, costly requirements before the water body has even been formally designated. This is especially true when the evidence required before a water body can be designated for one of the new beneficial uses is undefined, and no real criteria exist before such a decision can be made. Therefore, WSPA urges the Board to require amendment of the basin plans prior to any changes to permits are made to incorporate the new water quality objectives associated with the T-SUB, SUB, or CUL beneficial uses.

VII. Elimination of mixing under SIP for non-attainment water bodies

A. Industry will suffer a double hit in a reduction of effluent limitations, combined with disallowance of mixing or dilution factors allowed under the SIP

WSPA is concerned with what appears to be a severe limitation on dilution credits, and the fact that this limitation appears to be in direct conflict with the Board's

prior decision in Order WQ 2001-06, in which the Board found that a Section 303(d) listing alone was not a sufficient basis on which to conclude that a water body lacks assimilative capacity for an impairing pollutant. (Order WQ 2001-06, p 17).

In the Draft Provisions, the Board has expressly disallowed dilution "if the mercury concentration in fish tissue from fish in the receiving water exceeds the applicable MERCURY WATER QUALITY OBJECTIVES." (Draft Provisions, p A-11). This restriction is very similar to the automatic disallowance of dilution credits in the event of a Section 303(d) listing, which was struck down in Order WQ 2001-06. (Order WQ 2001-06, p 17, 20). In that Order, the Board agreed with petitioners that a 303(d)-listing was only suggestive, and not determinative of whether dilution credit was appropriate. (Order WQ 2001-06, p. 20) The Board stated that "[i]n assessing reasonable potential and developing effluent limitations, the Regional Water Board must review the available ambient data and base its determinations on this data." (Order WQ 2001-06, p 20)

The same must be said for the calculation of effluent limitations under the Draft Provisions. That is, the mere fact that the mercury concentration in fish tissue of fish in the receiving water exceeds the applicable objectives, does not eliminate the need for the Regional Water Board to assess water quality conditions, and in particular site-specific ambient data, in determining whether dilution credit is appropriate in the effluent limitation calculation.

Given this precedent and prior Board determination, WSPA requests that the Draft Provisions be amended to remove the blanket prohibition on dilution credit contained in IV.D.2.c.2). (Draft Provisions p A-11)

VIII. Failure to comply with CEQA

The Substitute Environmental Document (SED) portion of the Draft Staff Report purports to analyze the environmental impacts resulting from reasonably foreseeable means of compliance, as required by the California Environmental Quality Act (CEQA). Even in a programmatic review of a regulatory action that is intended to benefit the environment, CEQA requires a full and fair evaluation of its potential to result in adverse environmental side-effects. Such disclosure and analysis is necessary to inform the public, as the basis for informed decision-making, and to ensure that adverse impacts are reduced to the extent feasible by mitigation measures or alternatives.

In addressing the means of the compliance, the SED refers vaguely to "major facility upgrades" and "additional infrastructure" that will be needed for at least some number of publicly owned and industrial wastewater treatment facilities to comply with effluent limitations that will result from the new objectives. (*See, e.g.,* Draft Staff Report,

p. 177). Yet the SED fails to provide any description of the *type* of "major facility upgrades" that would be necessary. For the 12 ng/L effluent limitations associated with the least stringent new objectives, the SED states that it "is anticipated that major facility upgrades are unnecessary." (Draft Staff Report, p. 173). However, where major facility upgrades *are* anticipated to be necessary, to attain the 1 ng/L requirement, no upgrade technology at all is described. (Draft Staff Report, pp. 179-180). Moreover, as noted above and discussed in WSPA's technical comments, data from the Central Valley Regional Board indicate that tertiary treatment cannot achieve the 4 ng/L limit in all cases. A CEQA document cannot dismiss potentially significant impacts by relying on unsupported and optimistic assumptions.

Thus, the SED cannot assume that tertiary treatment will always suffice to achieve 4 ng/L, and in any case the SED does not claim – nor could it realistically do so – that tertiary treatment would suffice to achieve 1 ng/L. Yet the SED entirely omits discussion of means of compliance with the most stringent limits, which logically would be the most energy-intensive and would have the greatest environmental side-effects. This does not meet CEQA's mandate to identify and analyze reasonably foreseeable means of compliance with these objectives.

The SED also relies on there being "relatively few" wastewater/industrial treatment facility upgrades. (*See* table of impact assessment results for methods of compliance, Draft Staff Report, p. 193). Elsewhere, however, the SED states that it "is too difficult to anticipate how many faculties [sic] might need to upgrade as a result of the Subsistence Fishing Water Quality Objective" but goes on to acknowledge that only "27 percent of facilities statewide are meeting an annual average of 1 ng/L of mercury in their effluent." (Draft Staff Report, p. 243). CEQA analyses must be based on substantial evidence, but the evidence of the SED itself does not support reliance on the assumption that the magnitude of impacts will be limited to those from "relatively few" facility upgrades.

In addition to failing to disclose the nature and extent of necessary facility upgrades, the SED fails to address the reasonably foreseeable environmental impacts of their operation. Instead, the SED's analysis is almost entirely limited to the impacts of constructing the unspecified upgrades. (*See, e.g.,* Draft Staff Report, p. 190: "Upgrades would involve earth moving, construction activities, and heavy vehicle, equipment use"; *see also* pp. 202, 219-220). It goes without saying that the upgrades will need to be operated. Indeed, the Draft Staff Report does acknowledge in a single sentence in the greenhouse gas (GHG) section that "[t]he new facility may require more energy to operate, which could contribute more greenhouse gas emissions from the power generation, depending on the source of energy." (Draft Staff Report, p. 220). However, having recognized the issue, the SED inexplicably fails to include any further analysis of

operational impacts beyond that cursory sentence, and provides *no* analysis of any operational impacts for any issue other than GHG.

As noted above, information on which to base such analysis is readily available for the types of advanced treatment technologies that would be necessary for such upgrades. The Treatment Technology Report demonstrates that operation of these advanced treatment processes has potentially serious adverse environmental side-effects, including high energy consumption and increased greenhouse gas emissions. (Treatment Technology Report, p ES-2). Operation of advanced treatment technologies increase electrical energy usage at treatment facilities by a factor of 2.3 to 4.1 over baseline secondary treatment operations. (Treatment Technology Report, p. ES-4). Further, operation of MF/RO and electrical power sourcing result in direct and indirect greenhouse gas emission increases of at least 50–100% percent above baseline operations. (*Id.*) Addition of advanced treatment causes the daily energy demand to rise from a baseline of 10 megawatt hours per day to 22.7 megawatt hours per day for MF/GAC and 39.7 megawatt hours per day for MF/RO. (Treatment Technology Report, p. 35). The addition of MF/GAC causes greenhouse gas emissions to rise from under 3,000 megatons of CO2 equivalent per year to just under 5,000 megatons of CO2 equivalent per year and the addition of MF/RO results in an even more dramatic increase to over 7,000 megatons of CO2 equivalent per year. (Treatment Technology Report, p. 36).

Moreover, the Treatment Technology Report assumed that, to minimize the production of brine, treatment facilities should use zero liquid discharge ("ZLD") technology. (Treatment Technology Report, p. at 39.) However, this technology comes at a substantial cost of approximately $17.50 per gallon per day of ZLD capacity. (*Id.*) Without the costly ZLD technology, advanced treatment produces a substantial amount of brine. The highly concentrated brine must be properly disposed of to avoid adverse environmental impacts. Unless properly handled, discharges of brine to the environment can have significant impacts on biota and habitat, as the State Water Board is aware, having convened an expert panel to study "Management of Brine Discharges to Coastal Waters" in 2012. The SED does not evaluate or even mention environmental impacts associated with producing, managing and disposing of brine or other residuals, either as solid waste or potentially hazardous waste, or impacts to biological resources from disposal.

Further information is publicly available and could have been considered in the SED from studies of environmental impacts of RO and GAC technologies in other contexts, such as desalination plants and remediation projects. *See, e.g.*, Tularam and Ilahee, *Environmental concerns of desalinating seawater* (2007); and He, A *Calculation of the Environmental Footprint of a Granular Activated Carbon Regeneration Facility* (2012) (both attached to these comments for incorporation in the record). While some

impacts and aspects of such applications of the technology may not be relevant here, the SED did not even consider *any i*nformation on such environmental impacts of reasonably foreseeable means of compliance with the 1 ng/L limit or the 4 ng/L limit. As such, the SED fails as a CEQA informational document.

Without adequately evaluating the environmental impacts of treatment facility upgrades, the SED fails to fulfill the basic requirements for a CEQA document. The fact that the specific choice of technologies that individual POTWs and industrial dischargers may implement is uncertain at this stage does not mean that the need to implement *some* technology is speculative. Even in a programmatic analysis, environmental consequences of adopting the Draft Provisions that are reasonably foreseeable at the time of their adoption are ripe for CEQA review and cannot be deferred further to the future project level. The Draft Provisions constitute a commitment to implementation which must be carried out. Since they will be mandatory, other alternatives that could avoid or reduce such impacts will be rendered legally infeasible and precluded from consideration in future project level CEQA reviews. Since the addition of this information will necessarily reveal new or more severe environmental impacts from the operation of facility upgrades than those now discussed in the SED, the SED must be revised and recirculated to allow additional comment on such impacts.

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EXTERNAL MEMORANDUM

TO:	Kevin Buchan, Western States Petroleum Association
FROM:	Susan Paulsen, Ph.D., P.E., Principal Scientist, Director of Environmental & Earth Sciences Practice
DATE:	February 16, 2017
PROJECT:	1405218.000
SUBJECT:	Technical comments on the State Board's Mercury Provisions

This technical memorandum summarizes Exponent's comments on the State Water Resources Control Board's (Board's) proposed "Part 2 of the Water Quality Control Plan for Inland Surface Waters, Enclosed Bays, and Estuaries of California – Tribal and Subsistence Fishing Beneficial Uses and Mercury Provisions" (Mercury Provisions), which was released for public review on January 3, 2017.[1] Our comments fall into seven categories that may be summarized as follows:

1. Point source discharges subject to individual NPDES permits (e.g., industrial discharges) are small relative to other mercury sources; imposing stringent numeric effluent limitations will have little or no discernible effect on mercury concentrations in fish and the environment.

2. The proposed effluent limitations for non-stormwater individual NPDES dischargers may not be attainable (especially 1 ng/L).

3. Consistent with Board precedent, dilution credits and mixing zones should be allowed, if warranted by site-specific conditions, for NPDES discharges containing mercury.

4. Unless significant changes are made to the Mercury Provisions, the State Board should also implement a variance policy because, in many cases, the proposed water quality objectives will be unattainable.

[1] State Water Resources Control Board (SWRCB), 2016. "Draft Staff Report, Including Substitute Environmental Documentation, for Part 2 of the Water Quality Control Plan for Inland Surface Waters, Enclosed Bays, and Estuaries of California—Tribal and Subsistence Fishing Beneficial Uses and Mercury Provisions." January 3. Accessed February 6, 2017, at http://www.swrcb.ca.gov/water_issues/programs/mercury/docs/staff_report/hg_staff_report.pdf.

5. Mercury concentrations in many of the state's water bodies have exceeded the proposed objectives for decades or longer. As such, certain beneficial uses are not existing uses as defined by the Clean Water Act. The proposed Mercury Provisions should be modified to provide guidance regarding implementation measures and time schedules for "goal uses."

6. The proposed fish tissue objectives for the protection of human health and wildlife are likely too conservative, and the proposed water column targets are flawed. Neither the objectives nor the targets should be adopted at this time.

7. The implementation program in the State's proposed policy should be modified to focus on implementation actions that will lead to reductions in mercury in the state's waters and fish.

A detailed explanation of these comments is included below.

1. Point source discharges subject to individual NPDES permits (e.g., industrial discharges) are small relative to other mercury source;, imposing stringent numeric effluent limitations will have little or no discernible effect on mercury concentrations in fish and the environment.

In Appendix N of the Mercury Provisions, the Board presents source analysis data for the 14 existing mercury-related TMDLs in the state.[2] Only three of the mercury TMDLs for these water bodies list wastewater and industrial discharges as sources of mercury, and only two of them (for the Delta and San Francisco Bay) include a quantitative source analysis.[3] Appendix N indicates that wastewater and industrial discharges constitute 4% of methylmercury discharged to the Delta and 1.5% of total mercury discharged to San Francisco Bay.[4] Sources related to historical mining (tributaries and water body sediments) account for 93% and 82% of mercury in the Delta and San Francisco Bay, respectively, while atmospheric deposition (direct deposition and urban stormwater generated by mercury-laden precipitation) accounts for 15% of mercury in San Francisco Bay.

The Staff Report indicates that historical mining, natural soils, and direct deposition are "significant" and "major" sources of mercury.[5] The Staff Report notes that "the median and

[2] Appendix N. Wastewater and Industrial Discharges. Pp. N-14 to N-15. Note that Figure 3-1 (p. 33) of the Staff Report shows a map of mercury impaired waters on the 2012 303(d) list, which includes many more water bodies than those for which mercury TMDLs have already been developed.

[3] Appendix N, p. N-14.

[4] Appendix N, p. N-15.

[5] The Staff Report notes that "elevated mercury concentrations in present-day mine impacted waters and sediments indicate that hundreds to thousands of pounds of mercury remain at each of the many sites affected by hydraulic mining." (Staff Report at p. 47) The Staff Report also notes, "The Coast Ranges are naturally high in mercury… The soils in these areas that are naturally enriched with mercury erode, contributing to the mercury load in waterways… The mercury from mine waste, naturally enriched soils, and geothermal springs is a major source of mercury in the Coast Ranges, the Sierra Nevada Mountains, and also downstream in the Sacramento/San Joaquin Delta and San Francisco Bay." (Staff Report at p. 49) And finally, the Staff Report finds that "direct deposition

average mercury concentrations in rain in California were 6 ng/L and 12 ng/L" and "the 99.8th percentile of mercury concentrations in rain in the United States was 174 ng/L."[6,7] Thus, a significant fraction of rain samples in California would have concentrations higher than the proposed effluent limitations (explained below) for point source discharges. The Staff Report also indicates that "[m]ercury deposition from atmospheric emissions is thought to be the major source of mercury in some Southern California lakes and reservoirs (U.S. EPA 2012, Tetra Tech 2008)."[8] Finally, the Staff Report states, "[m]unicipal wastewater treatment plants are generally a relatively minor source of mercury to the environment compared to other sources. Wastewater treatment plants already remove most of the mercury from the effluent."[9]

Thus, data from the Mercury Provisions indicate that wastewater and industrial NPDES dischargers contribute little mercury to affected water bodies relative to other sources, suggesting that tight limitations on mercury from point sources will not result in significant reductions in environmental mercury concentrations. Further, the costs of imposing these requirements on industrial dischargers are not considered, nor are the "water quality conditions that could reasonably be achieved through the coordinated control of all factors which affect water quality in the area," as required by Section 13241 of the California Water Code.

2. The proposed effluent limitations for non-stormwater individual NPDES dischargers may not be attainable (especially 1 ng/L).

As discussed in Section 2 of the Staff Report, the proposed water quality objectives for mercury are expressed as fish tissue concentrations. These fish tissue concentrations are "translated" into water column concentrations that are proposed to be used to evaluate "reasonable potential" and to derive effluent limitations applicable to point source discharges. The water column concentrations and their proposed applicability to various WQOs and kinds of water bodies are summarized in Table 2.

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of mercury to water bodies (vs. deposition on land upstream) has been found to be very important in determining mercury levels in fish. Harris and colleagues applied isotopically labeled mercury (as $HgNO_3$) to a lake and the surrounding watershed. Essentially all of the increase in methylmercury in fish after 3 years was due to the mercury deposited directly to the lake surface… Furthermore, the results could suggest that controlling emissions that are deposited directly on the water surface may have a rapid effect (few years) on mercury level in fish (Harris et al. 2007)." (Staff Report at p. 50)

[6] Staff Report at p. 142.

[7] It has been widely demonstrated that precipitation in California has significant concentrations of mercury linked to coal-based Asian industrial emissions. For example, Steding and Flegal conclude that their study "demonstrates the impact of Asian industrial emissions on Hg concentrations in rain in western North America. The analyses substantiate previous reports on the influence of those emissions on Hg deposition in the North Pacific." (Steding, D.J. and A.R. Flegel. 2002. Mercury concentrations in coastal California precipitation: evidence of local and trans-Pacific fluxes of mercury to North America. J. Geophys. Res., 107 (2002):D24, p. 11-6.) They estimate mercury deposition via rainfall at approximately 25–50 nmol/year/m^2, which, if applied over the area of San Francisco Bay (approximated as 2,500 km^2), is roughly the same rate reported in the San Francisco Bay mercury TMDL for atmospheric deposition (74 g/day, from Table N-11).

[8] Staff Report at p. 49.

[9] Staff Report at p. 151.

The Staff Report asserts that the proposed 12 ng/L effluent limitation "is achievable" with existing secondary wastewater treatment technology and (possibly) a mercury source control/minimization program.[10] However, according to a recent study by HDR, typical mercury concentrations after secondary treatment range from 10 to 50 ng/L in industrial discharges.[11] The report does not examine the factors responsible for the variability in mercury concentrations in treated industrial effluent, though it likely depends in part on influent mercury concentrations. HDR's data suggest that some NPDES dischargers will *not* be able to meet the 12 ng/L effluent limitation with secondary treatment and/or a source control/minimization program.

Table 1. Proposed water column mercury concentrations for NPDES discharges and their applicability to various kinds of water bodies.

Total Hg water column concentrations	**Water quality objectives and water bodies to which water column concentration applies**
12 ng/L	Sport Fish and Wildlife WQOs in flowing water bodies
4 ng/L	Sport Fish and Wildlife WQOs in slow-moving water bodies; Tribal Subsistence Fishing (T-SUB) WQOs in flowing water bodies
1 ng/L	Tribal Subsistence Fishing (T-SUB) WQOs in slow-moving water bodies
Case-by-case determination	Subsistence Fishing (SUB) WQOs in any water body; Any WQOs in lakes and reservoirs

Source: State Water Resources Control Board (SWRCB), 2016. "Draft Staff Report, Including Substitute Environmental Documentation, for Part 2 of the Water Quality Control Plan for Inland Surface Waters, Enclosed Bays, and Estuaries of California—Tribal and Subsistence Fishing Beneficial Uses and Mercury Provisions." January 3. Pp. 173-183. Accessed February 7, 2017, at http://www.swrcb.ca.gov/water_issues/programs/mercury/docs/staff_report/hg_staff_report.pdf.

The Staff Report also asserts that the proposed 4 ng/L effluent limitation is achievable with tertiary treatment that includes nitrification/denitrification, but not with secondary treatment.[12] Data from the Central Valley Regional Board indicate that tertiary wastewater treatment can reduce mercury concentrations to 4 ng/L or below in at least some cases, but not in every case. For example, on average the San Jose/Santa Clara WWTP achieves a mercury concentration of 4 ng/L limitation using tertiary treatment,[13] while the Onondaga County WWTP does not.[14] Thus, it is likely that some dischargers already employing tertiary treatment will not be able to meet the 4 ng/L water column concentration.

In contrast with the 12 ng/L and 4 ng/L effluent limitations, the 1 ng/L effluent limitation proposed for slow-moving water bodies with a Tribal Subsistence Fishing designation is likely to be unachievable without extraordinary treatment upgrades and expenditures for most NPDES

[10] Staff Report, p. 174.
[11] HDR, 2013. Treatment Technology Review and Assessment. Association of Washington Business, Association of Washington Cities, Washington State Association of Counties. December 4, 2013. P. 7.
[12] Staff Report, p. 177.
[13] Central Valley Water Board, 2010. A review of methylmercury and inorganic mercury discharges from NPDES facilities in California's Central Valley Staff Report Final. March 2010. Rancho Cordova, CA. Table 2, p. 57.
[14] Central Valley Water Board, 2010. Table 5, p. 58.

dischargers. The treatment processes that would be needed to meet a concentration limit of 1 ng/L are not disclosed in the Staff Report. The Staff Report indicates that the 1 ng/L effluent limitation may be unachievable for NPDES dischargers not already achieving it (i.e., 73% of such dischargers according to Board data).[15] The Staff Report suggests no treatment methods for NPDES dischargers to meet the 1 ng/L effluent limitation. Instead, the Staff Report states, "the Water Boards may use compliance schedules, site-specific objectives (with extended compliance schedules), TMDLs, or variances if the [1 ng/L] effluent limitation is unachievable."[16]

HDR's review of treatment technologies states, "[t]here is limited information available about achieving ultralow effluent mercury concentrations near the 5 ng/L range."[17] The treatment process that appears most likely to be able to meet the proposed 1 ng/L effluent limitation is advanced treatment employing microfiltration and reverse osmosis (MF/RO), and then only under optimal conditions where input concentrations are low.[18] Under these circumstances, HDR found that dischargers could achieve mercury effluent concentration in the range of 1.2 to 3 ng/L.[19] However, this level of treatment and the associated substantial additional expenditures are not disclosed or examined in the Staff Report.

Appendix R of the Staff Report estimates the cost of upgrades from secondary to tertiary wastewater treatment that would be required by the policy to be in the range of $9–15 million/year over 20 years. Exponent believes this range significantly underestimates upgrade costs. For example, Sacramento Regional San—a POTW with a design flow rate of 181 million gallons per day (mgd)—is currently upgrading from secondary to tertiary treatment at a capital cost of approximately $2 billion and $50 million/year in operation and maintenance (O&M) thereafter.[20] These estimates for a single plant surpass the Appendix R total estimate for all plant upgrades in the state.

Given advanced treatment (e.g., MF/RO) will be necessary to achieve the 1 ng/L limitation, costs will be far higher. HDR suggests that the capital cost of upgrading a plant from secondary to advanced treatment (MF/RO) would be about $15–$162 per gallon per day (gpd) of treatment capacity, depending on the size of the plant to be upgraded,[21] or one to two order of magnitude higher than the Appendix R estimate of $1.14 per gpd to upgrade to tertiary treatment.[22] Clearly, the costs required to upgrade a treatment plant to advanced treatment will exceed the costs to

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[15] Staff Report at p. 180: "Based on statewide monitoring data for all facilities that may be impacted by the Provisions, it is estimated that eight facilities would not meet the new effluent limits for the [T-SUB] water quality objective in flowing water bodies and will have to undergo a major treatment plant upgrade if they are designated with the T-SUB beneficial use in the future." And from the Staff Report at p. 182: "Recent data from discharger self-monitoring reports indicates [sic] that about 73 percent of all discharges to waters include in the geographic scope of the Provisions exceeded 1 ng/L, based on 2009-2015 data."

[16] Staff Report at p. 183.

[17] HDR, 2013, p. 12.

[18] HDR, 2013, p. 13.

[19] HDR, 2013, pp. 13-14.

[20] Data accessed February 8, 2017, from http://www.regionalsan.com/echowater-project.

[21] HDR. 2013. p. ES-2.

[22] Appendix R, Economic Analysis. R-47.

upgrade to tertiary treatment, such that the costs of implementing the SWRCB's proposal will be far greater than disclosed in the Staff Report.

Although the Staff Report presents some analysis of anticipated costs for wastewater treatment plants, the Staff Report does not appear to include any discussion of the control measures or costs that may be required for industrial facilities with individual permits to meet the proposed effluent limitations.[23] For facilities regulated under the industrial general permit (IGP), the Staff Report states that existing control measures may not be sufficient to meet the proposed revised Numeric Action Limits (NALs)[24] but does not analyze the treatment processes that could be employed to meet the NALs, and does not discuss the associated costs.

3. Consistent with Board precedent, dilution credits and mixing zones should be allowed, if warranted by site-specific conditions, for NPDES discharges containing mercury.

The draft Staff Report states in parts that the Regional Boards have discretion to grant dilution credits and/or mixing zones in NPDES permits for discharges containing mercury. For example, the Staff Report states, "Water Boards have the discretion to allow dilution credits where appropriate."[25] The Staff Report discusses the permissibility of dilution credits most frequently when acknowledging the difficulty that NPDES dischargers may have attaining proposed mercury effluent limitations. For example, in discussing the difficulty of meeting the proposed 1 ng/L effluent limitation for mercury-containing discharges to slow-moving waters designated as supporting the Tribal Subsistence Fishing beneficial use (T-SUB), the Staff Report states, "However, if the Water Board exercises its discretion to allow dilution credits, the objective would be much more achievable."[26]

However, at other points the Staff Report indicates that dilution credits will not be allowed under most circumstances. The Staff Report indicates that dilution credits will not be allowed for water bodies that are included on the list of impaired waters (303(d) list) for mercury.[27] SWRCB Staff also indicated at the January 9th, 2017, workshop that dilution credits and mixing zones would not be allowed in NPDES permits for water bodies that are impaired for mercury. The Staff Report also indicates that the following language would be included in Chapter IV of the ISWEBE Plan (the Implementation Chapter): "Dilution shall be prohibited if the mercury concentration in fish tissue from fish in the receiving water exceeds the applicable MERCURY WATER QUALITY OBJECTIVES."[28] Presumably, this prohibition would apply regardless of whether a water body is on the 303(d) list of impaired waters for mercury.

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[23] Staff Report Appendix R, R-23.

[24] Appendix R, R-40.

[25] Staff Report, p. 10.

[26] Staff Report, p. 180. See also a similar statement on p. 182.

[27] "...the Water Boards have the discretion to allow dilution credits *in waters that currently meet the applicable water quality standards...*," (at p. 174) and "if the Water Boards exercise discretion to allow dilution credits *in waters achieving the applicable water quality standard(s)*, the effluent limitations would be much more achievable" (at p. 177) (emphasis added).

[28] Staff Report at p. 304; capitals in original.

The Board's position that dilution credits will not be allowed in water bodies that are impaired for mercury appears to contradict precedential Board Orders, including Order 2001-06. The Board issued Order 2001-06 after its review of petitions filed regarding two NPDES permits issued by the San Francisco Bay Regional Water Quality Control Board (SF Board). The permits regulated industrial discharges from two refineries that discharge to Suisun Bay and San Pablo Bay, on either side of the Carquinez Strait. In the initial NPDES permits, the SF Board did not allow mixing zones or dilution credits when it calculated effluent limitations for the discharges, asserting that since both Suisun Bay and San Pablo Bay were on the 303(d) list for several bioaccumulative toxic pollutants, the receiving waters did not have assimilative capacity for those pollutants, and thus dilution credits should not be allowed in the calculation of effluent limitations.

However, upon review the State Board found that, in fact, dilution credits should be allowed in these cases. The Board's decision was based, in part, on a study by Flow Science Incorporated (Flow Science) that demonstrated the large amounts of dilution available in the receiving waters due to the large daily tidal flows into and out of the Delta via Carquinez Strait.[29] Flow Science concluded that tidal flushing in this region of the Bay-Delta system is substantial,[30] and that far-field long-term average dilution of discharges at these locations was roughly 3,000:1. Flow Science also concluded that "[e]ven for the bioaccumulative pollutants of dioxin, PCBs, 4,4-DDE, and dieldrin, there is no evidence that indicates that discharges from the [refinery] diffuser are in any way responsible for elevated concentrations in receiving waters, sediments, or biota. Similarly, there is no evidence … that enforcing the effluent limits proposed in the tentative order for these constituents would result in any discernible decrease in concentrations of these constituents in receiving waters, sediments, or biota. Any decision to set effluent limits of these constituents as proposed in the tentative order cannot be justified on scientific mass balance principles… these arguments also lead to the conclusion that there is no scientific reason for denying a dilution credit for these pollutants."

Following its review, the State Board remanded the two permits to the SF Board for appropriate revision. The summary for Order 2001-06 states that "A Regional Water Quality Control Board (Regional Water Board) cannot rely solely on a Section 303(d) listing as the basis for concluding that a receiving water lacks assimilative capacity for an impairing pollutant. Rather, the Regional Water Board must base assimilative capacity determinations on the relevant water quality-related data."[31] As the information supporting Order 2001-06 suggests, relevant water quality-related data include the dilution available for the discharge, whether the discharge makes a significant contribution of pollutants to the receiving water relative to other sources (e.g., non-

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[29] Flow Science (2001). Comments on proposed tentative order renewing NPDES Permit CA0005789 NPDES SUPPORT PERMIT CA0005789 CONTRACT NO. RB 0101-12. Letter from Susan C. Paulsen to Kevin Buchan, Western States Petroleum Association. October 31.

[30] Although these discharges are to an estuary/enclosed bay system, the receiving water at the discharge locations is not "slow moving" and significant dilution is available. The State Board should provide additional guidance regarding the site-specific assessment of whether a discharge is to a "slow moving" or "flowing" water body.

[31] Summary for Board water quality Order 2001-06, accessed February 9, 2017, at http://www.waterboards.ca.gov/board_decisions/adopted_orders/water_quality/wqo01.shtml.

point sources), and whether or not effluent limitations would affect concentrations in the receiving water, sediments, or biota in a significant way.

Given precedential Order 2001-06, the Board may not rely solely on a Section 303(d) listing to determine assimilative capacity and the permissibility of a dilution credit. The proposed Mercury Provisions should be revised to require the consideration of site-specific information and to allow dilution credits in cases where a discharge is minor relative to other sources, and where effluent limitations would not have a significant effect on receiving water, sediment, or fish tissue concentrations.

4. Unless significant changes are made to the Mercury Provisions, the State Board should also implement a variance policy because, in many cases, the proposed water quality objectives will be unattainable.

On August 21, 2015, U.S. EPA published water quality standards regulation (80 FR 51010), which includes water quality standards variances (40 CFR § 131.14). This regulation authorizes states to implement variances in cases where the highest attainable condition of the receiving water does not meet the applicable water quality standard. In such cases, the variance becomes the water quality standard used by permitting authorities in generating effluent limitations for discharges regulated by NPDES permits.

Given that the proposed Mercury Provisions, as currently written, require mercury effluent limitations that are likely unattainable for certain dischargers and water bodies (see below), the use of variances by Regional Boards is necessary to prevent chronic violation of permit terms and inordinate penalties associated with such violation. Although the State Water Board has proposed a statewide Variance Policy in association with its adoption of water quality standards for bacteria, there is currently no established statewide mechanism for water quality standards variances; only the Central Valley Regional Board has adopted a variance for salinity.[32] As discussed throughout these comments, Exponent recommends that the proposed Mercury Provisions be modified so that effluent limitations are not required when they would not produce a discernible reduction in mercury concentrations in receiving waters or fish tissue. However, if the State Board elects not to make these changes, the State Board should adopt a statewide variance policy *concurrently* with the Mercury Provisions.

5. Mercury concentrations in many of the state's water bodies have exceeded the proposed objectives for decades or longer. As such, certain beneficial uses are not existing uses as defined by the Clean Water Act. The proposed Mercury Provisions should be modified to provide guidance regarding implementation measures and time schedules for "goal uses."

[32] See Public Scoping Meeting for the Proposed Statewide Water Quality Standards Variance Policy (Jan. 23, 2017); Amendments To The Water Quality Control Plan For The Sacramento River And San Joaquin River Basins And The Water Quality Control Plan For The Tulare Lake Basin To Add Policies For Variances From Surface Water Quality Standards For Point Source Dischargers, Variance Program For Salinity, And Exception From Implementation Of Water Quality Objectives For Salinity, Resolution No. R5-2014-0074

The Clean Water Act defines an existing use such that it requires both (1) that the activity has occurred since November 28, 1975, and (2) that the water quality has been sufficient to support the beneficial use since that date. State Board staff confirmed that the State Board interprets existing uses using this definition, and that by this definition, many "existing uses" designated in the State's Basin Plans are not existing uses as defined by the Clean Water Act; State Board staff also clarified that the water boards have the discretion to allow longer compliance schedules for past, present, or probable future beneficial uses as designated pursuant to the requirements of the Porter-Cologne Act (California Water Code).[33] Although the Staff Report states that "beneficial uses may be designated as a goal use (or probable future use in Porter-Cologne parlance) where neither the water quality is currently being attained or the use is actually occurring, but there is evidence to indicate that the use would be a probable future use,"[34] the Staff Report does not discuss the additional implementation options that should be available for uses that are "goal uses" as opposed to existing uses under the Clean Water Act.

As noted in the Staff Report, mercury concentrations in many of the state's water bodies have been affected since well before November 28, 1975, by a range of sources, including historic mining, atmospheric deposition, natural geology. Historic mining activity, in particular, has affected many of the region's water bodies since approximately the mid-1850s.[35] For this reason, concentrations of mercury in fish tissue have exceeded the proposed tissue concentrations for the commercial and sportfishing (COMM), subsistence (SUB), and tribal subsistence (T-SUB) beneficial uses in much of the state for more than one hundred years. Thus, in many cases these beneficial uses cannot be considered to be beneficial uses under the Clean Water Act, and extended compliance schedules, plus other implementation mechanisms as discussed in these comments, should be considered by the State Board.

Exponent respectfully suggests that the Staff Report and Mercury Provisions should be revised to provide guidance on the designation of proposed beneficial uses, and to identify and provide guidance on the range of implementation actions that will be necessary to achieve meaningful reductions in mercury concentrations in the state's waters and fish.

6. The proposed fish tissue objectives for the protection of human health and wildlife are likely too conservative, and the proposed water column targets are flawed. Neither the objectives nor the targets should be adopted at this time.

The proposed fish tissue objectives for the protection of human health were derived based on multiple conservative assumptions about exposure and toxicity that compound to make the objectives unreasonably low. For example, the proposed fish tissue concentrations for COMM

[33] At the January 9, 2017, State Board workshop on the proposed Mercury Provisions, Rik Rasmussen stated that "if they call it an existing use in the basin plan, it's not necessarily an existing use under federal law, it's subject to refinement… There's nothing to prevent the water boards, if they designate a beneficial use as a probable future beneficial use, to either (a) have a different water quality objective as they do it, or (b) have a longer implementation schedule and say 'hey, it's a probable future use, we don't expect this to be met for 50 years'." (Transcribed from video of the January 9, 2017 workshop.)

[34] Staff Report at p. 112.

[35] Staff Report at pp. 45-55.

and T-SUB were derived using EPA's old default average body weight value (70 kg)[36], rather than the revised default average body weight (80 kg) used in a later document.[37] Using the old body weight (70 kg) rather than the revised default weight (80 kg) drives down the fish tissue concentration. EPA has used the new default body weight (80 kg) to revise human health criteria for several chemicals,[38] but not for methylmercury.

The fish tissue objectives derived for the protection of wildlife are also likely overly conservative. For example, interspecies and NOAEL-to-LOAEL[39] uncertainty factors were applied by USFWS to derive the avian reference dose of 0.021 mg/kg/day used in computing the proposed wildlife objectives.[40] However, a critical review paper by Fuchsman et al. (2017) suggests that the reference dose of 0.021 mg/kg/day may be too conservative.[41] Based on the current literature, Fuchsman et al. propose values between 0.05 mg/kg/day to 0.5 mg/kg/day on a dose basis as suitable for risk assessment. These values are two to 20 times higher than the proposed reference dose, resulting in unreasonably low fish tissue objectives.

Finally, the proposed water column concentration targets (noted above: 12 ng/L, 4 ng/L, and 1 ng/L) were derived using a methodology that is flawed in several ways. Most importantly, the concentration targets were derived using inappropriate bioaccumulation factors (BAFs). Board Staff used two national BAFs to calculate mercury water concentration targets for every water body in California. National BAFs are calculated as the geometric mean of field-measured BAFs obtained from published literature,[42] and range over two to three orders of magnitude due to variability between the many different regions and water bodies. As this broad range suggests, BAFs are site-specific; there is potential for mercury methylation and bioaccumulation to vary significantly from location to location and over time (seasonally). Even within California, conditions vary considerably between regions. As a result, national or statewide default values are likely to be inaccurate on a site-specific basis.

Given the overly conservative and flawed nature of the proposed fish tissue objectives and water column targets, neither set of numbers should be adopted at this time.

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[36] U.S. EPA. 2000. Methodology for Deriving Ambient Water Quality Criteria for the Protection of Human Health (2000). EPA-822-B-00-004. October 2000. Office of Water, Office of Science and Technology, U.S. Environmental Protection Agency, Washington DC.

[37] U.S. EPA. 2015a. Fact Sheet: Human Health Ambient Water Quality Criteria: 2015 Update. U.S. Environmental Protection Agency, Washington DC. https://www.epa.gov/sites/production/files/2015-10/documents/human-health-2015-update-factsheet.pdf. Accessed February 8, 2017.

[38] U.S. EPA. 2015b. Table Comparing EPA's Updated 2015 Final Human Health Criteria to Previous Criteria. U.S. Environmental Protection Agency, Washington DC. https://www.epa.gov/sites/production/files/2015-10/documents/comparison-of-epa-s-2015-final-updated-human-health-awqc-and-previous-awqc-june-2015.pdf. Accessed February 8, 2017.

[39] "NOAEL": No observed adverse effect concentration; "LOAEL": Lowest observed adverse effect concentration.

[40] USFWS (U.S Fish and Wildlife Service). 2003. Evaluation of the Clean Water Act Section 304(a) Human Health Criterion for Methylmercury: Protectiveness for Threatened and Endangered Wildlife in California. October. Sacramento Fish and Wildlife Office, Environmental Contaminants Division, Sacramento, CA.

[41] Fuchsman, P.C., Brown, L.E., Henning, M.H., Bock, M.J., Magar, V.S. 2017. Toxicity reference values for methylmercury effects on avian reproduction: Critical review and analysis. Environ Toxicol Chem 36(2):294–319.

[42] USEPA. 2010. Guidance for Implementing the January 2001 Methylmercury Water Quality Criterion. EPA 823-R-10-001. U.S. Environmental Protection Agency, Office of Water, Washington, DC.

7. The implementation program in the State's proposed policy should be modified to focus on implementation actions that will lead to meaningful reductions in mercury in the state's waters and fish.

As detailed throughout these comments and as acknowledged in the Staff Report, non-point sources (including historical mines, atmospheric deposition, and mercury in natural soil and sediments) are the primary sources of mercury in the State's waters and in fish. For this reason, controls on point sources are not expected to result in a meaningful difference in mercury concentrations in most water bodies. Despite this fact, the proposed Mercury Provisions focus almost exclusively on implementation measures for point sources.

Although the proposed Mercury Provisions include language stating that the permitting authority is authorized to exempt certain dischargers from some or all of the provisions of the policy if the discharge is found to be "insignificant (de minimis),"[43] it appears that this provision would have very limited application and that stringent mercury effluent limitations would be required for almost all NPDES permits. As noted above, the proposed effluent limitations will be difficult to achieve and are likely to require significant expenditures of resources by NPDES permittees, particularly POTWs and industrial dischargers. Also as noted in Comment 6, the method used in the Staff Report to calculate water column targets from tissue objectives (i.e., the use of national BAFs) does not recognize the complex and site-specific behavior of mercury in the environment, and is likely to lead to effluent limitations that are not appropriate in specific water bodies.

For point sources, the State Board should consider developing alternatives to effluent limitations for mercury. If effluent limitations continue to be required, the State Board should adopt, concurrently, a statewide Variance Policy[44] to be implemented where water quality standards cannot be achieved within a reasonable timeframe. Consistent with the State Board's Order No. 2001-006, site-specific factors should be assessed in determining both the need for effluent limitations and the methods by which those limitations, if needed, should be calculated. The State Board should develop guidance on the following:

- site-specific information that should be used to assess whether point source controls will have a significant impact on mercury concentrations in water and fish
- the information that should be used to determine if a discharge is to "slow moving" waters
- the use of mixing zones and dilution credits (see also Comment 1)
- clear guidance regarding the distinction between existing and "goal" uses, and the implementation measures that would apply to each (see Comment 3)
- the use of extended compliance schedules for "goal uses."

[43] Staff Report at p. 153.

[44] We recognize and appreciate that the State Board is in the process of developing a statewide Variance Policy, as noticed on January 13, 2017. However, this policy is scheduled to be adopted after the Mercury Provisions and is being adopted in the context of water quality objectives for indicator bacteria. A Variance Policy is needed with the Mercury Provisions as currently proposed, because the effluent limitations identified in the draft policy are likely not achievable, and will likely not result in meaningful reductions in mercury in the environment.

Exponent respectfully suggests that the State Board's proposed Mercury Provisions offer an opportunity to identify and implement alternative measures for mercury control. Alternative measures should be investigated and discussed in public workshops prior to adoption of the proposed Provisions, and offer the best (perhaps the only) chance to achieve meaningful reductions in mercury concentrations in the environment. Alternative implementation measures that should be considered include, but are not limited to:

- a program for trading or offsets
- a "water funds" approach to regional or watershed-based mercury control measures
- engaging other state agencies in efforts to control non-point sources (e.g., engaging the Air Resources Board in efforts to control atmospheric sources of mercury)
- programs to address non-point sources.

The most effective approaches to mercury control will be those that identify implementation actions for the primary sources of mercury. The implementation measures currently identified in the proposed Mercury Provisions do not effectively target these primary sources, and the State's proposed Mercury Provisions should be revised accordingly.

CALIFORNIA ENVIRONMENTAL PROTECTION AGENCY

REGIONAL WATER QUALITY CONTROL BOARD
CENTRAL VALLEY REGION

A Review of Methylmercury and Inorganic Mercury Discharges from NPDES Facilities in California's Central Valley

Staff Report

FINAL

March 2010

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EXECUTIVE SUMMARY

Fish in the Sacramento-San Joaquin River Delta Estuary (Delta) have elevated levels of methylmercury that pose a risk for human and wildlife consumers. As a result, the Delta is on the Clean Water Act Section 303(d) List of Impaired Water Bodies.
Section 303(d)(1)(A) of the Clean Water Act requires the Central Valley Water Board to develop a water quality management strategy – a.k.a. total maximum daily load (TMDL) – to lower fish mercury levels in the Delta so that the beneficial uses of fishing and wildlife habitat are attained.

Although methylmercury is less than 1% of all mercury discharged to the Delta, methylmercury is the chemical that accumulates in the food web. Available science indicates that reducing methylmercury in ambient water is the most direct way to reduce methylmercury in biota. The need for methylmercury effluent data for facilities permitted by the National Pollutant Discharge Elimination System (NPDES) program arose during the development of the TMDL source analysis for the Delta. There was a substantial amount of concentration and load data for inorganic mercury; however, there was limited information about methylmercury. Although inorganic mercury in effluent is a concern because of the potential for it to be methylated in downstream aquatic ecosystems, methylmercury also is a concern because it is immediately available for uptake by aquatic biota.

The Central Valley Water Board issued a California Water Code Section 13267 Order (13267 Order) in 2004 that required municipal wastewater treatment plants (WWTPs) and other non-municipal NPDES-permitted dischargers located in the Delta and its source region to monitor their methylmercury discharges. Effluent methylmercury data were submitted by 111 facilities. Although not required by the 13267 Order, thirty-six of those facilities also submitted influent methylmercury data. In addition, the Sacramento Regional Count Sanitation District submitted influent and effluent methylmercury concentration data for a six-year period.

This report provides a literature review and summary of NPDES influent and effluent methylmercury and inorganic mercury data along with available treatment process information for municipal WWTPs. No policy or regulation is either expressed or intended. This report is not a required element of the Delta methylmercury TMDL. However, this report includes a wealth of effluent and influent data and treatment process information that may be useful for future characterization and control studies in the Central Valley and elsewhere nationwide.

Overall, NPDES facilities account for about 4% of the methylmercury load to the Delta; NPDES facilities within the Delta contribute about 205 grams per year (g/year) while facilities in upstream watersheds that are downstream of major dams contribute about 24 g/year. The Delta TMDL divides the Delta into hydrologically-defined subwatershed

areas; different sources supply the different areas. For example, NPDES facilities within the San Joaquin River and Sacramento River subareas contribute about 7-9% of all methylmercury loading to those subareas, while NPDES facilities within the Central Delta, West Delta, and Yolo Bypass subareas contribute less than 0.2% of all methylmercury loading to these subareas. This report evaluates how the different NPDES categories contribute to methylmercury loading to the Delta.

Twelve categories of non-municipal facilities submitted effluent data: aggregate, aquaculture, drinking water treatment, food processing, groundwater remediation, heating/cooling, manufacturing, mines, paper/saw mill, power generation, power generation/domestic WWTP and a miscellaneous category. A few of the aquaculture and power generation facilities were neither significant sources nor sinks of methylmercury. More influent and effluent data are necessary to determine if other facilities in these two categories and heating/cooling facilities are net methylmercury sources or sinks. Aggregate, drinking water treatment, groundwater remediation, paper/saw mills and the other non-municipal facilities were sources of methylmercury but typically had low effluent methylmercury concentrations (average of 0.05 nanograms per liter [ng/l]). Eight of the twelve categories of non-municipal facilities had average effluent methylmercury concentrations less than or equal to 0.05 ng/l (the lowest calibration standard for methylmercury). Of the 198 effluent methylmercury samples submitted by all non-municipal facilities, 134 were less than or equal to 0.05 ng/l, and 80 of those were below the method detection limit (typically < 0.025 ng/l). The highest effluent methylmercury concentration observed at a non-municipal facility was 1.19 ng/l from a stormwater detention pond at the Sierra Pacific Industries Shasta Lake Mill, which is in the paper/saw mill category; all other samples from the paper/saw mills and other non-municipal facilities were less than 0.2 ng/l.

In contrast, municipal WWTPs contribute the most discharge (by discharge volume and methylmercury load) to the Delta source region of any one of the NPDES discharger categories monitored and have the most variability in effluent methylmercury concentrations. Individual effluent samples collected from WWTPs had methylmercury concentrations that ranged from below the detection limit to 4 ng/l, a 200-fold difference. Twenty of the 61 WWTPs that submitted effluent data had an average concentration less than or equal to 0.05 ng/l, and 13 of the WWTPs had an average concentration less than 0.03 ng/l. In contrast, 18 WWTPs had an average effluent methylmercury concentration greater than 0.2 ng/l, and seven had mean concentrations greater than 1 ng/l.

Staff grouped the municipal WWTPs into mutually exclusive treatment categories based on their secondary, tertiary and disinfection treatment types to determine if trends existed between treatment processes and effluent methylmercury concentrations. The facilities that use treatment pond systems (oxidation, facilitative, settling or stabilization ponds) had the highest effluent methylmercury concentrations. The median effluent

methylmercury values of all pond treatment categories were statistically higher than all other treatment categories, with one exception; the “Pond + Filtration + Chlorination/Decholorination” category did not have significantly higher effluent methylmercury concentrations than the “Secondary + Chlorination/Decholorination” (secondary treatment without nitrification/denitrification and filtration) category. WWTPs that use one or more of the following treatment processes generally had lower effluent methylmercury concentrations: nitrification/denitrification, filtration, and ultraviolet (UV) disinfection. Treatment categories that include one or more of these processes had statistically lower effluent methylmercury concentrations than both the pond and “Secondary + Chlorination/Dechlorination” categories.

Seasonal variability was observed in effluent methylmercury concentrations at several municipal WWTPs in the Central Valley and elsewhere. Studies were conducted at the City of Winnipeg WWTP (Canada) and Onondaga County WWTP (New York); both WWTP studies demonstrated that effluent methylmercury concentrations increase as ambient temperatures increase, particularly when treatment ponds are used. Effluent methylmercury concentrations were also higher in the warm season (e.g., May through November) than the cool season at several of the Central Valley WWTPs. The Central Valley WWTPs that showed seasonal patterns in their effluent methylmercury concentrations had many different types of treatment processes, indicating that there was no trend between the type of treatment process and seasonality.

These and other possible trends between treatment processes and effluent methylmercury concentrations identified by the Central Valley facility data and literature reviews merit additional investigation. There are many factors that affect the concentrations of methylmercury in effluent and subsequent methylation/demethylation processes in the receiving waters. Additional studies are required to understand the mercury/methylmercury relationships between different treatment processes and mercury methylation/demethylation processes in the receiving water. Chapter 5 of this report suggests preliminary ideas for future analyses and key questions to be addressed by treatment plant analyses.

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ACRONYMS

Basin Plan	Central Valley Region Water Quality Control Plan for the Sacramento River and San Joaquin River Basins
CTR	California Toxics Rule
CVRWQCB	Central Valley Regional Water Quality Control Board (a.k.a. Central Valley Water Board)
CWA	Federal Clean Water Act
EC	Electrical conductivity
GIS	Geographic Information System
GW	Groundwater
Hg	Mercury
ID	Irrigation District
mgd	Million gallons per day
MeHg	Monomethyl mercury (also referred to as methylmercury in this report)
NPDES	National Pollutant Discharge Elimination System
O	Oxygen
PUD	Public Utilities District
SD	Sanitation District
SFBRWQCB	San Francisco Bay Regional Water Quality Control Board (a.k.a. San Francisco Bay Water Board)
SFEI	San Francisco Estuary Institute
SRCSD	Sacramento Regional County Sanitation District
TMDL	Total maximum daily load
TSS	Total suspended solids
USEPA	U.S. Environmental Protection Agency
UV	Ultraviolet radiation
WTP	Water treatment plant (drinking water filtration or groundwater treatment)
WWTP	Wastewater treatment plant
WY	Water Year[1]

[1] A "water year" (WY) is defined as the period between 1 October and 30 September of the following year; for example, WY2001 is the period between 1 October 2000 and 30 September 2001. The California Department of Water Resources (DWR) developed the Hydrologic Classification Index (HCI) to evaluate the distribution of wet and dry years in the Central Valley. DWR classifies water year types according to the natural water production of the major basins. See the following website for more information about the HCI: http://cdec.water.ca.gov/cgi-progs/iodir/WSIHIST

UNITS OF MEASURE

μg	microgram
μg/g	microgram per gram
μg/l	microgram per liter
μm	micrometer
cfs	cubic feet per second
cm	centimeter
g	Gram
g/day	gram per day
g/l	gram per liter
in/yr	inches per year
kg	kilogram
L	Liter
m	Meter
mg	milligram
mg/g	milligram per gram
ml	milliliter
mm	millimeter
ng	nanograms
ng/l	nanograms per liter
o/oo	parts per thousand (salinity)
ppb	parts per billion; usually μg/kg
ppm	parts per million; usually mg/kg or μg/g
ppt	parts per trillion; usually ng/kg

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1 INTRODUCTION

In 1990, the Central Valley Regional Water Quality Control Board (Central Valley Water Board) identified the Delta as impaired by mercury because fish had elevated levels that posed a risk for human and wildlife consumers. This is a concern because fishing is a popular activity in the Delta. About 300,000 licensed sport and subsistence anglers fish in the Delta each year, along with an unknown number of unlicensed anglers. Wildlife species of concern that consume Delta fish include California least tern, bald eagle, and river otter. Eating fish with high levels of mercury is a problem, especially for the young, because mercury is a potent neurotoxicant that impairs nervous systems in both humans and wildlife (National Research Council (NRC), 2000). In addition, it affects their reproductive and immune system function; examples of negative effects include deficits in memory and motor control in humans and reductions in physical abilities in wildlife (Wolfe *et al.*, 1998; Whitney, 1991 in Huber, 1997; Dansereau *et al*., 1999; Huber, 1997; Wiener and Spry, 1996).

As stated in CalFed's 2003 Mercury Strategy: "The problem with mercury in the Delta's aquatic ecosystems can be defined as biotic exposure to methylmercury." Methylmercury is the most toxic and bioaccumulated form of mercury. Methylmercury concentrations in aquatic ecosystems are the result of two competing processes: methylation and demethylation. Methylation is the addition of a methyl group to an inorganic mercury molecule. Sulfate reducing bacteria in sediment are the primary agents responsible for the methylation of mercury in aquatic ecosystems. Maximum methylmercury production occurs at the oxic-anoxic boundary in sediment, usually several centimeters below the surface. Although less common, methylmercury also may be formed in anaerobic water (Regnell *et al.*, 1996 and 2001).

Demethylation is both a biotic and abiotic process. Both sulfate reducing and methanogen-type bacteria have been reported to demethylate mercury in sediment with maximum demethylation co-occurring in the same zone where maximum methylmercury production is located (Marvin-DiPasquale *et al*., 2000). Photodegradation of methylmercury in the water column also has been observed (Sellers *et al*., 1996; Byington *et al*., 2005; Gill, 2008). The rate of both biotic and abiotic demethylation appear quantitatively important in controlling net methylmercury concentrations in aquatic ecosystems (Sellers and Kelly, 2001; Marvin-DiPasquale *et al*., 2000; Foe *et al*., 2008).Several published papers provide comprehensive reviews of the methylmercury cycle in the Delta and elsewhere (e.g., Wiener *et al.*, 2003a and 2003b; Tetra Tech, Inc., 2005; Larry Walker Associates (LWA), 2002). Board staff and others have found that in some waterways, processes of methylmercury production and transport downstream in the water column are dominant (e.g., in the lower Sacramento and San Joaquin Rivers upstream of the Delta) and in others, processes that remove

methylmercury from the water column such as photodegradation and sedimentation are dominant (e.g., in the Central Delta) (Stephenson *et al.*, 2008).

Once in the water column, methylmercury bioaccumulates in the food web. That is, very low methylmercury levels in water lead to high methylmercury levels in fish. For example, largemouth bass in the Delta have more than 6 million times the methylmercury as the water in which they swim. As a result, human and wildlife exposure to methylmercury is primarily through consumption of fish and shellfish, rather than drinking water.

Although processes that remove methylmercury from the water column may be dominant in some water bodies, there is no information that suggests that methylmercury discharged into a water body would disappear so rapidly that none of it would be accumulated, at least in part, into the food chain immediately downstream of the discharge. For example, in its Localized Mercury Bioaccumulation Study, SRCSD concluded that SRCSD WWTP effluent contributes about the same percentage of methylmercury to Sacramento River biota downstream of its discharge as it does to the methylmercury loading in the river. SRCSD found that four out of six fish and clams species sampled had methylmercury concentrations about 10% greater downstream from the discharge than upstream. The ratio of SRSCD WWTP methylmercury loads to river methylmercury loads was also about 10% during the study period. Also, as demonstrated by extensive spatial and temporal sampling of large and small fish in the Delta and its tributary watersheds (e.g., Slotton *et al*., 2003 and 2007; Davis *et al*., 2000, 2003 and 2008), methylmercury persists long enough in tributary and Delta waters to be reflected in fish uptake with regional patterns that stay consistent over years.

Although methylmercury is less than 1% of the inorganic mercury input to the Delta (Wood *et al*., 2010b), methylmercury is the form of mercury that accumulates in the food web. Available science indicates that reducing methylmercury in ambient water is the most direct way to reduce methylmercury in biota. Methylmercury produced by many modern-day activities may potentially be managed so that less methylmercury is discharged. Chapters 3 and 5 in the February 2008 draft staff TMDL report (Wood *et al*., 2010b) provides information about the relationship between methylmercury in Delta fish and water and potentially controllable methylation processes in the Delta region. Methylmercury in Delta waterways comes from many sources, such as wetlands, agricultural drains, urban runoff, wastewater treatment plant effluent and tributary inflows, in addition to methylmercury production in and flux from open-water sediments in Delta waterways.

Section 303(d)(1)(A) of the federal Clean Water Act requires States to establish a “Total Maximum Daily Load” (TMDL) for each impaired water body to attain water quality standards. Section 13240 of the State of California Porter-Cologne Water Quality

Control Act requires Regional Boards to develop water quality control plans to meet reasonable protection of beneficial uses, including establishing water quality objectives and a program of implementation to achieve the water quality objectives. A TMDL represents the maximum load (usually expressed as a rate, such as kilograms per day (kg/day) or other appropriate measure) of a pollutant that a water body can receive and still meet water quality objectives. A TMDL describes the reductions needed to meet water quality objectives and allocates those reductions among the sources in the watershed. Central Valley Water Board staff has proposed a mercury TMDL control program for the Delta that addresses sources of both inorganic mercury and methylmercury (Wood *et al.*, 2010a and 2010b). The proposed program focuses on methylmercury source reduction because available information indicates that methylmercury levels in water may be a primary factor determining methylmercury concentrations in fish. A inorganic mercury load reduction strategy also is part of the proposed program for several reasons: to reduce sediment mercury levels and associated water methylmercury levels in the Delta; to maintain compliance with the USEPA's criterion of 50 ng/l; and to comply with the San Francisco Bay mercury control program adopted by the San Francisco Bay Regional Water Quality Control Board.

The need for methylmercury data for discharges permitted by the National Pollutant Discharge Elimination System (NPDES) arose during the development of the source analysis for the Delta methylmercury TMDL. At the beginning of the TMDL development, only one NPDES-permitted facility in the Central Valley had collected effluent methylmercury data. Between December 2000 and June 2003, the Sacramento Regional County Sanitation District (SRCSD) collected 60 samples to characterize its effluent methylmercury levels. In February and March 2004, Central Valley Water Board staff conducted two sampling events at four other municipal facilities to determine whether the SRCSD data are representative of other WWTPs. The 2004 sampling results, along with data available in the published literature, indicated that the effluent methylmercury data for the SRCSD facility might not be representative of all facilities in the Delta. Therefore, the Central Valley Water Board issued a California Water Code Section 13267 Order (13267 Order) in 2004 that required NPDES dischargers, including municipal WWTPs and non-municipal facilities to monitor methylmercury discharges for one year.

Specifically, the 13267 Order required the following:

- Instantaneous, unfiltered grab samples collected from the facilities effluent for one year (generally September 2004 to August 2005) at a monthly, quarterly or biannual frequency, depending on facility size and whether there was a discharge to surface water;
- Use of clean hands/dirty hands sampling procedures and U.S. Environmental Protection Agency (USEPA) Method 1630/1631 (Revision E) with a method detection limit of 0.02 ng/l;

- Analysis of a matrix spike and matrix spike duplicate with either the first or second set of samples to ensure an acceptable methylmercury recovery rate; and
- Analysis of a travel blank with every other set of samples.

The 13267 Order did not require the collection of inorganic mercury data. However, if the facility was already collecting samples for inorganic mercury analysis, then it was required to collect the methylmercury samples concurrently. Also all inorganic mercury data and any other methylmercury monitoring data collected by a facility must be reported to the Central Valley Water Board. While not required by the 13267 Order, collection of instantaneous grab samples from the facilities' upstream receiving water and main influent were recommended to calculate methylmercury treatment efficiency. Appendix A provides an example of the 13267 Order letter and a list of facilities that received the Order.

This technical staff report presents a summary of the methylmercury data submitted by the NPDES dischargers. Because of the file size, data for individual facilities are not attached to this report; a Microsoft Excel file containing all data is available upon request. This report also includes an evaluation of the quality assurance/quality control results, a literature review, a description of the treatment processes in place at the municipal WWTPs when their methylmercury data were collected, a discussion of treatment processes and their possible relation to effluent methylmercury levels, and recommendations for further research. An administrative draft report was sent in December 2008 to all of the NPDES facilities whose data was summarized in this report. Staff addressed comments submitted for the December 2008 draft report and made the revised draft report available for public review in May 2009. Staff incorporated corrections and comments on the December 2008 and May 2009 draft reports into this final version of the report. Comments submitted by facilities and staff responses are in Appendix D.

As part of the proposed Delta mercury control program (Wood *et al.*, 2010a), Central Valley Water Board staff is currently recommending that methylmercury dischargers in the Delta and its source region conduct collaborative methylmercury control studies to develop methods to reduce their methylmercury discharges. This report and the associated database are a first step in that process, particularly for the municipal WWTPs.

The literature review of studies that investigated methylmercury in WWTPs is presented in Chapter 2. The quality assurance/quality control evaluation is presented in Chapter 3. The summary of effluent and influent methylmercury data is provided in Chapter 4. In response to comments from the Sacramento Regional County Sanitation District on the May 2009 draft report, an additional chapter (Chapter 5) was added to this report to assess the relative contribution of methylmercury load to the Delta by NPDES facilities in and upstream of the Delta. The discussion of treatment processes

and their possible relation to effluent methylmercury levels and recommendations for further research are provided in Chapter 6.

In this report, mercury, inorganic mercury, and total mercury are used synonymously.

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2 LITERATURE REVIEW

Several published reports have evaluated wastewater treatment plant mercury fate and transport. Results and conclusions from these studies are summarized below and in Table 1.

2.1 San Jose / Santa Clara Water Pollution Control Plant

From October 2004 to March 2006, the City of San Jose conducted a sampling program to study the fate and transport of mercury within its wastewater treatment facility in compliance with its NPDES waste discharge permit (SJ/SC, 2007). The treatment process of the San Jose/Santa Clara Water Pollution Control Plant (SJ/SC WPCP) consists of screening and grit removal, primary sedimentation, secondary treatment (activated sludge with nitrification/denitrification), secondary clarification, filtration, chlorination, and dechlorination before the wastewater is discharged. During the secondary treatment process the waste stream is split between two parallel units, which are identical in function. Aqueous samples were collected from the raw influent after grit removal, primary effluent, settled sewage influent to nitrification units (secondary influent), secondary effluent, tertiary filter influent and effluent, and final effluent. City staff collected and analyzed over 140 aqueous samples for total and dissolved mercury, methylmercury, and parallel samples for total suspended solids (TSS), sulfide, chloride, and sulfate. Total and dissolved mercury and methylmercury results for the aqueous sampling are summarized in Table 2.

In addition, City staff collected and analyzed 32 biosolids samples for inorganic mercury, methylmercury, sulfide, sulfate, pH and moisture content. Sludge samples were collected from the primary sludge, waste activated sludge from secondary units, returned activated sludge, thickened activated sludge and digested sludge. Inorganic mercury concentrations in sludge were higher than in the water due to the strong particle association of mercury. Inorganic mercury and methylmercury concentrations in sludge were roughly uniform throughout the treatment process.

In this study, the removal of TSS corresponded with the removal of inorganic mercury. Raw influent contained approximately 190 mg/l TSS and 168 ng/l inorganic mercury. After primary settling, the TSS concentration was approximately 85 mg/l and the inorganic mercury concentration was 92 ng/l. Secondary effluent, which is a combined flow from identical and parallel activated sludge units, continued to show a close correlation between TSS and inorganic mercury removal with concentrations of about 5 mg/l and 5.2 ng/l, respectively. The TSS was reduced to approximately 2 mg/l in the treated tertiary effluent, but increased to 3 mg/l in the final effluent. The corresponding inorganic mercury concentration for the tertiary treated effluent was 1.6 ng/l, and for the final effluent was 2.0 ng/l. The study states that this slight increase in inorganic mercury

and TSS in the final effluent may be attributed to the addition of the filter backwash water, treated by flocculation and clarification, to the filter effluent prior to disinfection. The final effluent represented an overall removal of 99% of the inorganic mercury.

The secondary treatment process proved to be a catalyst for the removal of methylmercury, indicated by a primary effluent concentration of 1.5 ng/l and a reduction to 0.05 ng/l in the secondary effluent. Although anoxic conditions are present during some process steps of secondary treatment, the conditions were not sufficient to promote methylation of mercury. The authors of the study noted that little apparent sulfate reduction occurred within the treatment process, which could explain why significant methylation did not occur. Final effluent concentrations of methylmercury showed a decrease to 0.04 ng/l, representing an overall removal efficiency of 97%.

The study found no significant seasonal trend in influent inorganic mercury concentrations; however, the study observed a diurnal trend, with higher concentrations in the afternoon and early evening. There were no observed diurnal patterns for methylmercury in the influent. The study concluded that methylmercury concentrations in the influent were relatively uniform over the course of a day. The study did not discuss seasonal or diurnal patterns or variability in effluent inorganic mercury and methylmercury concentrations.

2.2 Sacramento Regional County Sanitation District Wastewater Treatment Plant

The Sacramento Regional County Sanitation District (SRCSD) WWTP is a 181 mgd pure oxygen activated sludge secondary treatment plant (Parmer *et al.*, 2005). The SRCSD also operates a 5 mgd tertiary treatment plant for water recycling. The SRCSD study investigated both inorganic mercury and methylmercury fate and transport for the wastewater and solids treatment trains. The tertiary effluent (recycled water) was not tested. This study used a two-phased approach, identified as Phase 1A and 1B.

Phase 1A included nine sampling days that occurred from October to November 2004. Samples were taken from the influent, primary effluent, secondary effluent prior to chlorination, dechlorinated final effluent, and solids storage basin return flow to the plant influent structure. The liquid supernatant from the digested sludge and three different solids storage basins (SSB) named green, black and harvest were also sampled. The parameters measured in Phase 1A were inorganic mercury (total and dissolved), methylmercury (total and dissolved), total dissolved solids, TSS, pH and dissolved oxygen.

Phase 1B involved more extensive sampling of the treatment process from the end of Phase 1A to May 2005. Phase 1B sampling locations included all locations sampled in Phase 1A, except for the supernatant from the SSB Ponds. In addition, the mixed liquor (mixture of the influent flow to the secondary clarifiers and the return activated sludge),

the waste activated sludge from the secondary clarifiers, the biosolids recycling facility (BRF) influent from the sludge digesters and the BRF return flow to the plant influent structure were sampled during Phase 1B. The same analytes were measured in both Phases 1A and 1B. The concentrations, mass loads and particulate concentrations for the inorganic mercury and methylmercury samples collected during both phases of the study are summarized in Tables 3 and 4.

There was a strong correlation between solids removal and inorganic mercury removal. The inorganic mercury concentration was reduced by an average of 94% from the influent to the secondary effluent, and 95% from the influent to the final dechlorinated effluent. The TSS was reduced by an average of 95% from the influent to the secondary effluent, and 96% from the influent to the final effluent. Overall, it appeared that the treatment process removed inorganic mercury more efficiently than methylmercury. The methylmercury concentration was reduced by an average of 75% from the influent to the secondary effluent, and 70% from the influent to the dechlorinated final effluent.

The highest methylmercury loading in the liquid train of the plant occurred in the mixed liquor channel, which comprises primary effluent and 40% return activated sludge. The highest methylmercury concentration (not including digested sludge and return flows) of about 31 ng/l occurred in the return activated sludge stream, which is recycled to the mixed liquor (activated sludge unit process). The secondary process achieved the greatest reduction of methylmercury concentrations and loads in the liquid train as observed from the primary and secondary effluents; however, it also had the greatest methylmercury concentration (in the waste activated sludge stream) of all the liquid train unit processes in this study.

An increase in methylmercury concentration occurred between the secondary effluent (0.38 ng/l) and the dechlorinated final effluent (0.55 ng/l). The study authors noted the increase was consistent with the slightly increased TSS concentration in the final effluent. According to the authors, no backwash or other return flow is added to the waste stream between the secondary effluent and the dechlorinated final effluent. The report authors concluded that both inorganic mercury and methylmercury removals correlated with TSS removal due to strong particle affinity.

2.3 Concentrations and Fluxes of Inorganic mercury and Methylmercury within the Onondaga County Metropolitan Wastewater Treatment Plant

The Onondaga County Metropolitan Wastewater Treatment Plant discharges its effluent to Onondaga Lake, a mercury-contaminated lake in Syracuse, New York (McAlear, 1996). A study at the Onondaga County Metropolitan WWTP investigated the concentrations and fluxes of inorganic mercury and methylmercury within the plant and in its discharge. The WWTP treatment processes consist of screening and grit removal,

primary clarification, conventional activated sludge, secondary clarification, chlorination, and phosphorous removal (coagulation by addition of iron salts followed by clarification) before the wastewater is discharged.

Monthly samples were collected from the plant influent, primary effluent, secondary effluent, “tertiary” effluent from the phosphorous removal clarifiers and final plant effluent between October 1995 and September 1996 and analyzed for inorganic mercury and methylmercury. Daily composite total dissolved solids concentrations and daily inorganic mercury concentrations in sludge also were evaluated. The average concentrations of inorganic mercury, methylmercury and TSS at each treatment process are summarized in Table 5.

The authors determined that seasonal conditions play an important role in the methylation process, and in particular, that warm temperatures may be a catalyst for methylation. The influent methylmercury concentrations were much lower during cold weather (November through April) than during warm weather (May through October), and further, methylmercury concentrations remained relatively constant throughout the treatment process during cold weather (Table 6). However, during the warm weather months, an increase in the average methylmercury concentrations occurred between primary effluent and secondary effluent (from 1.8 ng/l to 3.5 ng/l), followed by a decrease in the “tertiary” and final effluents (2.9 ng/l and 1.6 ng/l, respectively). Despite this apparent methylation during secondary treatment in warm weather months, the study found that the average final effluent methylmercury concentration in the warm weather months was only slightly higher than during the cold weather months (1.6 ng/l compared to 1.4 ng/l).

There was a strong correlation between the mean concentrations of inorganic mercury and TSS throughout the treatment processes. In contrast, a weak correlation was evident between the mean methylmercury and TSS concentrations. The ratios of methylmercury versus inorganic mercury concentrations for the entire study period (includes warm and cold weather months) were highest during secondary treatment at 20.5%, decreasing to 8.3% in the final effluent.

During the cold weather months, November through April, the influent and final effluent methylmercury averaged 2.3 and 1.4 ng/l, respectively. Primary and secondary treatment effluent had concentrations near 2.0 ng/l. The highest methylmercury concentration during the cold weather months was in the “tertiary” effluent (2.4 ng/l). The percentage of inorganic mercury as methylmercury during the same period increased gradually throughout the treatment process from about 1% (influent), 2% (primary), 6% (secondary), and 12% (“tertiary”), before decreasing in the outfall to 3%.

The influent and final plant effluent methylmercury averaged 7.8 and 1.6 ng/l, respectively, in the warm weather months. The percentage of inorganic mercury as

methylmercury during warm weather months varied from approximately 2 to 3% in the influent and primary effluent, to a high of 35% in secondary treatment, and then decreasing to 15% in tertiary treatment and 13% in the final effluent measured at the outfall. Although activated sludge is an aerobic treatment process, the study author hypothesized that methylation of mercury likely occurred during secondary treatment in anaerobic microenvironments.

2.4 City of Winnipeg, Manitoba, Canada

The City of Winnipeg, Manitoba operates three secondary treatment plants that discharge to two local rivers, the Red and Assiniboine Rivers (Bodaly *et al.*, 1998). Two of the plants (the North End and South End plants) use pure oxygen activated sludge in their secondary treatment process. The West End plant, in contrast, uses conventional activated sludge with diffusers. The West End facility also is the only WWTP of the three to use lagoons after secondary treatment and before final effluent discharge.

Samples were collected from the influent and effluent of the three plants. Five sampling events took place from early summer to autumn 1994 and one event took place in spring 1995, for a total of six sampling events. The unfiltered water samples were analyzed for inorganic mercury and methylmercury.

Influent methylmercury concentrations observed at the three treatment plants ranged from 0.5 to greater than 4 ng/l and averaged 2.2 ng/l. Effluent methylmercury concentrations observed at the North and South End plants ranged from 0.13 to 0.56 ng/l. However, effluent methylmercury concentrations observed at the West End Plant, which utilizes conventional activated sludge and lagoons after secondary treatment, were significantly higher, varying from about 0.2 to greater than 2 ng/l. A seasonal trend was apparent only in the West End facility; effluent methylmercury concentrations increased as ambient temperatures increased, with the highest concentration occurring in August. The authors noted that the high concentrations of methylmercury in 1994 may have been related to the fact that the West End facility had begun operations within the year and experienced start-up problems. Also, this facility was the only one of the three plants to use final polishing lagoons, which could be sites of substantial methylmercury production, especially if anoxic conditions exist.

Overall removal rates for the three treatment plants were 88% of inorganic mercury and 90% of methylmercury. However, this methylmercury removal rate does not include the summer period at the West End Plant when methylmercury concentrations in the effluent were elevated. The study authors did not observe a seasonal pattern in the concentration of inorganic mercury in effluent from any of the plants.

2.5 Fritz Island Wastewater Treatment Plant

The City of Reading signed a consent decree with the State of Pennsylvania agreeing to remove three mercury-filled trickling filter center column seals used in the Fritz Island WWTP (Gilmour and Bloom, 1995). This allowed researchers to examine the extent of inorganic mercury and methylmercury contamination within the plant and its receiving water body, the Schuylkill River. Each filter seal initially contained 340 kg of mercury, some of which was lost from the seals due to excessive pressure and equipment failures and escaped to the rock media and underbed of the trickling filters. The mobility and fate of the mercury contaminating the Fritz Island WWTP was determined by evaluating inorganic mercury and methylmercury concentrations of the inflow to and outflow from a number of individual treatment components in the WWTP.

The Fritz Island WWTP is a secondary treatment facility that employs trickling filters (TFs) for secondary treatment. The treatment process consists of primary settling before the 1st stage TFs, 1st stage trickling filters (TF# 1-3), intermediate settling before the 2nd stage TFs, 2nd stage trickling filters (TF# 4-6), settling after the 2nd stage TFs, aeration and then a final settling process. There are six trickling filters involved in the treatment process. Four of these (TF# 1, 3, 5 and 6) originally used mercury-containing center seals. The contaminated seal in trickling filter #5 was replaced with a mechanical seal in 1984, and the rock media and underbed was cleaned or replaced.

Researchers collected aqueous samples from the plant influent and effluent, and sludge samples from the belt press, from July to December 1993. The aqueous and sludge samples were analyzed for inorganic mercury and methylmercury. A summary of the inorganic mercury and methylmercury concentration data and calculated mass balances are presented in Tables 7 and 8, respectively. During a one-time sampling event in August 1993, researchers collected inorganic mercury and methylmercury samples from the inputs and outputs from each treatment process within the WWTP. A summary of those results is provided in Table 9.

With the exception of TF# 5, all of the trickling filters were measurable sources of both inorganic mercury and methylmercury, demonstrated by greater concentrations in the effluent than in the influent of the contaminated trickling filters. In TF# 1, the inorganic mercury concentration of the effluent was 25 times higher than the influent, and the methylmercury concentration was four times higher. Inorganic mercury in the wastewater was lost to the sludge during the settling steps. More than 90% of the inorganic mercury in the effluent of the first stage trickling filters was removed to the sludge during the intermediate settling process. A similar trend was observed in the post 2nd stage and final settling processes.

An average of 157 grams of inorganic mercury was released from the plant per day, with less than 10% in the effluent and more than 90% released in the sludge. Only

about 20 grams of the 157 grams was derived from the plant influent, with the remainder generated inside the plant. However, the WWTP was an overall sink for inorganic mercury in the wastewater, demonstrated by lower inorganic mercury concentrations and loads in the plant effluent than in the plant influent.

Methylmercury production was closely related to the mercury concentration in each of the trickling filters. The contaminated trickling filters were the main sites of methylmercury production. Methylmercury concentrations decreased during aeration, which the study authors hypothesized was attributed to chemical or microbial demethylation of methylmercury to inorganic mercury during this process. Overall, about 0.4 g/day of methylmercury was released from the plant, with about 25% of this amount introduced from the plant influent and the rest generated inside the plant. Of the 0.4 g/day of methylmercury released from the plant, 30% was in the sludge, and 70% was released to the river in the effluent. The WWTP was an overall source of methylmercury in the wastewater. Both the methylmercury concentrations and loads in the effluent were higher than in the plant influent.

2.6 Whitlingham Sewage Treatment Works

Between May 1986 and June 1988, a study was conducted at Whitlingham Sewage Treatment Works in Norwich, England to evaluate the behavior of heavy metals during wastewater treatment and to investigate the occurrence of mercury methylation throughout the treatment plant (Goldstone *et al.*, 1990). The wastewater treatment processes at the Whitlingham facility consisted of primary clarification followed by secondary activated sludge treatment before discharge as effluent.

The study consisted of two sampling events, the first in May 1986 and the second in October 1987. The constituents evaluated during both sampling events were inorganic mercury, dissolved mercury, total solids and total suspended solids (TSS). Methylmercury was sampled throughout the treatment process only during the second sampling event. Raw sewage (influent), settled sewage (primary effluent), picket fence thickener overflow, returned activated sludge, and final effluent were sampled during the second event. Table 10 provides a summary of the inorganic mercury and methylmercury concentration results for the second sampling event.

Methylation of mercury within the treatment plant was observed, especially in the presence of bacterial solids. Methylmercury and inorganic mercury concentrations were highest in the return activated sludge. However, the average methylmercury concentration of the final effluent was below the 10 ng/l detection limit; the study authors assumed that the seven samples with methylmercury concentrations below the detection limit were equal to zero when they calculated the average methylmercury concentration of the final effluent.

The effects of centrifugation and filtration on additional return activated sludge samples were investigated to determine whether methylmercury has a greater affinity for the soluble or particulate phase of the return activated sludge. Results indicated that methylmercury was predominantly associated with solids. The study authors determined that the absence of detectable methylmercury in the influent and primary effluent indicates that all methylmercury in the return activated sludge had been produced by *in situ* biological methylation. However, the authors noted that the aerobic conditions of the activated sludge could be considered unfavorable to the production and accumulation of methylmercury. The authors hypothesized that the high concentrations of bacterial solids and other organic material in the waste activated sludge may have outweighed the aerobic conditions and permitted the establishment of an equilibrium concentration of methylmercury. Correlations performed on the data confirmed a relationship between high concentrations of biological solids and aerobic methylation.

2.7 Determination of Methylmercury in a Pilot-Scale Activated Sludge Wastewater Treatment Plant

Pavlogeorgatos and others (2006) investigated methylation in a pilot-scale activated sludge plant supplied with synthetic wastewater enriched with mercury. The wastewater was spiked with mercury concentrations of 10, 100 and 500 µg/l. The initial methylmercury concentration of the synthetic wastewater was not evaluated. Duplicate samples from the aeration tank, treatment plant effluent, and sludge were analyzed for inorganic mercury and methylmercury. The results indicated that all of the samples had methylmercury concentrations below the detection limit of 0.07 µg/l. The highest inorganic mercury concentration of 17.8 mg/l was found in the sludge sample associated with the 500 µg/l mercury spike. On average, 82.8% of the mercury entering the treatment plant was adsorbed to the particulate matter in the aeration tank.

While no conclusion could be drawn regarding methylation because of the high method detection limit (0.7 µg/l, compared to the MDL of 0.02 ng/l required for the 13267 Order monitoring), this investigation confirmed that the reduction and volatilization of mercury is the primary pathway to its removal. In the aeration tank, this pathway becomes secondary when the microorganisms and mercury reach equilibrium. Adsorption of mercury onto the biosolid flocs becomes the primary removal mechanism. The study theorized that methylmercury was not detectable because the conditions were aerobic, or because demethylation predominated. Methylation may have occurred but was not detectable given the method detection limit used in the study. The authors also discovered that spiking the wastewater with increased mercury concentrations reduced the removal effectiveness of organic matter in the treatment process.

3 QUALITY ASSURANCE AND QUALITY CONTROL

The 13267 Order required NPDES facilities to submit effluent methylmercury monitoring data collected using the clean hands/dirty hands technique described in USEPA Method 1669 and analyzed using USEPA Method 1630/1631 (Revision E) with a method detection limit (MDL) of 0.02 ng/l. In addition, the facilities were required to have a matrix spike/matrix spike duplicate (MS/MSD) performed on their first or second set of effluent samples, and travel blanks performed with every other set of samples. The MS/MSD is designed to determine if the effluent matrix causes interferences in methylmercury recovery and to provide an estimate of analytical precision. The travel blank is used to determine if there is any contamination during transport. Other quality assurance/quality control (QA/QC) parameters not required by the 13267 Order but evaluated by some of the facilities include field duplicates, MS/MSD of other matrixes, and field blanks. Staff used guidelines described in the CALFED Mercury Program Quality Assurance Project Plan (Puckett, 2000) to assess the quality of the data presented in this report.

3.1 Method Detection Limit

Since Frontier GeoSciences laboratory has a minimum reporting limit of 0.025 ng/l and Frontier conducted many of the analyses for the facilities, staff considered non-detects to be reported as less than 0.025 ng/l or lower. Only on six occasions were MDLs greater than 0.025 ng/l; the maximum MDL reported was 0.05 ng/l. The concentration data submitted by the dischargers overall appear to be of high quality and analyzed by laboratories able to perform the latest methods for analyzing methylmercury.

3.2 Sample Handling and Preservation

USEPA Method 1630 requires samples to be preserved with acid within 48 hours to a pH of less than two. The analytical laboratories verify the pH of the samples upon receipt, and the laboratories acid-preserve the samples if the pH is found to be greater than two. The laboratories flag samples when the samples are preserved after the 48-hour hold time. Thirty-four percent of the samples analyzed for methylmercury were preserved before being received by the analytical laboratories (field), 37% were preserved at the laboratories, and 29% of the samples had no acid preservation information provided (unknown). All data from samples known to have pH hold time exceedences were flagged so. Data for samples whose hold times exceeded 60 hours were flagged and excluded from calculations made in this report. Table 11 shows the data for these excluded samples. All samples with no preservation information provided were assumed to meet their pH hold times and their data were accepted.

Twenty-two samples exceeded the 48-hour hold time, and of those, 21 samples exceeded 60 hours (Table 11). Acid preservation stops the bacterial activity in the water that produces methylmercury from inorganic mercury. Samples without preservation may not be representative of the conditions at the time of sampling if bacterial activity continues after sampling. However, because bacterial activity is believed to be minimal in samples that are kept cold (0 to 4°C), data from samples with minimal hold time exceedences (<60 hours) were considered acceptable.

The USEPA Method 1630 states that unpreserved samples should be kept at 0 to 4°C until preserved, after which samples can be stored at cool temperatures. The analytical laboratory reports state the optimal temperature is 4 ±2°C for unpreserved samples; as a result, all data derived from samples received by the laboratories above 6°C and unpreserved were flagged for being out of optimal temperature range. A review of the data indicated that temperature did not likely affect the samples; therefore, staff incorporated the flagged data in this report's calculations.

3.3 Matrix Spike/Matrix Spike Duplicates

MS/MSD results were submitted by 93 facilities (see Appendix C, Table C.1). The facilities were not required to submit the laboratory reports from the analysis laboratories; consequently, eight facilities submitted summaries only of their methylmercury data. Ninety-two facilities had MS/MSDs performed on their effluent at least once for a total of 161 effluent MS/MSDs performed. On eight occasions, the MS/MSDs were not within the criteria of acceptability.[2] For three events the MS/MSD had relative percent differences (RPD) greater than 25%, and the associated effluent data were flagged "not reproducible" for high variability. In addition, there were three times where the MS/MSD had recoveries below 70% and twice the recovery was greater than 130%, hence the associated effluent data were flagged "low bias" for low recoveries and "high bias" for high recoveries, respectively.

Influent and receiving water had MS/MSDs performed on 25 and 32 occasions, respectively. One of the influent MS/MSDs exhibited a recovery above 130%, and the data were flagged "high bias". Five of the influent MS/MSDs (20% of the MS/MSDs performed on influent samples) exhibited recoveries below 70%, and their data were flagged "low bias". The USEPA Method 1630 may underestimate the methylmercury concentration in wastewater influent samples. Receiving water MS/MSD experienced recoveries below 70% once and above 130% once, hence the associated data were flagged accordingly. In all instances that the MS/MSDs experienced recoveries below 70% or above 130%, the laboratories' analyses of laboratory control samples were

[2] Acceptable MS/MSD recovery per the CalFed QAPP: >70% and <130% recovery. Acceptable MS/MSD RPD: ≤25%.

within acceptable limits, indicating that the laboratories performed the method appropriately.

One laboratory reported that high levels of chloride in effluent could interfere with recoveries, and that a special preparation of the sample could remedy the problem. However, the small occurrence of low recoveries in effluent indicates that there is little interference caused by the effluent matrix. In addition, the low occurrence of MS/MSD RPD exceedences greater than 25% indicates the high precision of the laboratory analyses and the high quality of data produced.

3.4 Travel Blanks

The facilities were required to submit travel blanks with every other set of samples submitted. Some facilities submitted trip blanks or field blanks, in addition to or instead of travel blanks. Travel blanks are bottles filled with deionized (DI) water that are transported to the site but not opened (CDFG, 2002). Travel blanks are synonymous to trip blanks, which is defined by USEPA as, "A clean sample of a matrix that is taken from the laboratory to the sampling site and transported back to the laboratory without being exposed to the sampling procedures" (USEPA, 2002). Conversely, one of the laboratories contracted to collect water samples defined trip blanks as, "…Trip blanks should be handled the same as the sample; however, they only need to be exposed to the atmosphere. Do not put sample in the bottle. Trip blanks are designed to measure the amount of methyl mercury in the air…" This suggests that this laboratory's trip blanks were performed to test parameters typically assessed with field blanks. Field blanks are considered acceptable substitutes because they assess contamination introduced by field sampling conditions in addition to all of the contamination assessed by travel blanks.

Approximately 85% of the facilities that submitted data fulfilled their requirements for blanks submittal, 4% partially fulfilled their requirements, and 11% did not submit any blank analysis. Approximately 5% of the combined number of trip and field blanks had methylmercury concentrations detected above the MDL; however, the majority of the detections were less than two times the detection limit or less than five times the sample concentration. These deviations are not considered to affect the quality of the sample concentration data. The analytical laboratories reported that concentration detections less than two times the MDL have high variability and are considered estimates. Only 3% of the blank concentration detections were greater than two times the MDL and proportionately high when compared to their respective sample concentrations. Because these data could be affected by contamination they were flagged. Blanks are designed to be used as an interactive QA/QC tool, where sources of reoccurring contaminations can be identified and eliminated. Because most of the contaminations

were isolated events, the concentration data accuracy should not be greatly affected; therefore, the flagged data were used in this report's calculations.

3.5 Field Duplicates

Field duplicates are used to examine field homogeneity and sampling handling. Though not required by the 13267 Order, field duplicates were collected on 35 occasions (Table 12). Field duplicate mean RPD was 12.7%. On four occasions the RPD was greater than 25%; however, the methylmercury concentrations for each of the samples and their duplicates were less than 10 times the MDL. Sample concentrations at or near the MDL have higher variability, suggesting that these field duplicates' high RPD cannot be completely attributed to field variability. All of the field duplicates met the criterion for data acceptability, indicating that the facilities performing field duplicates had acceptable field collection precision. Field duplicates were not incorporated into the calculations of this report.

3.6 Anomalous Values

Several anomalous values were observed in the methylmercury and inorganic mercury dataset when compared to the remainder of the values observed at a facility (Table 13). When an analytical laboratory report was available, staff was able to confirm the anomalous values. None of the available laboratory reports indicated that contamination or any other error or misreporting occurred. Otherwise, if no laboratory information was provided, staff assumed that all data including anomalous values were correct. As a result, Board staff included all anomalous values in the report calculations since staff could not conclude definitively that errors were made.

SRCSD staff identified three methylmercury results that failed their quality assurance review. Influent and effluent samples collected on 13 July 2001 had methylmercury concentrations of 1.05 and 2.93 ng/l, respectively; SRCSD staff commented in their data review notes, "highly unlikely that there is more MeHg in effluent than influent". Likewise, an effluent sample collected on 18 June 2006 had a methylmercury concentration of 0.077 ng/l; SRCSD noted, "highly unlikely that effluent concentration is this low". As a result, these three samples were not included in the calculations in this report.

There were three instances when a municipal WWTP had a higher effluent methylmercury concentration than the influent value collected on the same day. This occurred one time at each of the Colusa, SRCSD Walnut Grove and Mariposa WWTPs. Staff carefully reviewed available information to determine the likelihood of some type of data or reporting error. The influent and effluent values were confirmed by analytical

laboratory reports and chain of custody documents; hence, staff assumed that the data was correct and the data was included in the report calculations.

3.7 Summary

The data presented in this report meets the overall QA/QC requirements of the NPDES 13267 Order. Less than 1% of the analyses for methylmercury had method detection limits greater than 0.025 ng/l, with 0.05 ng/l being the highest, indicating that the samples were analyzed using the latest methods. Only 3% of the effluent matrix spikes resulted in recoveries exceeding the criterion, and less than 2% of the MS/MSD analyses resulted in RPDs greater than 25%. Wastewater treatment plant effluent appears to exhibit little to no interference with Method 1630. These results agree with Caltest Analytical Laboratory staff's review of Method 1630 performance on wastewater they have analyzed, where their last 200 matrix spikes averaged 93% recovery in matrix and MS/MSD relative percent differences averaged 9% in their last 100 MS/MSD performed (SFEI, 2007). In contrast, 20% of the MS/MSD performed on influent samples submitted by Central Valley facilities exhibited low recoveries; therefore, Method 1630 may underestimate the methylmercury concentration in wastewater influent samples. Less than 3% of the combined travel and field blanks resulted in detections above the criterion of acceptability, suggesting that there was little cross contamination between bottles and/or contamination from field procedures.

Twenty-five methylmercury samples were excluded from calculations and graphs in this report. Twenty-two of these excluded samples had acid preservation hold times that exceeded 60 hours. In addition, 6 of the samples excluded due to hold time exceedences, were also contaminated with mercury in the laboratory and were not believed to be representative of site influent or effluent. These contaminated samples were from General Electric Co. GWCS (NPDES No. CA0081833) and were collected on 18 October 2004. The three other methylmercury samples excluded from calculations in this report failed the SRCSD staff quality assurance review.

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4 REVIEW OF METHYLMERCURY CONCENTRATION DATA FROM CENTRAL VALLEY DISCHARGERS

There are currently 124 NPDES-permitted dischargers in the Delta source region[3] representing a variety of discharger types, primarily: aggregate, aquaculture, food processing, heating/cooling, manufacturing, mines, municipal WWTPs, paper/saw mills, power generation, water filtration (e.g., for drinking water), and groundwater remediation. The approximate discharge volumes of each of these NPDES categories are provided in Table 14.

A total of 134 Central Valley NPDES-permitted dischargers received the 13267 Order (see Appendix A, Table A.1). Staff did not send the 13267 Order to every NPDES-permitted discharger in the Delta source region. In addition, some of the facilities that received the Order discharge upstream of major dams, some were not discharging to surface waters during the study period, and some no longer discharge. Of the 134 dischargers that received the Order, 18 facilities discharge upstream of major dams, 22 facilities discharge directly to the Delta/Yolo Bypass, 17 discharge to other waterways that are 303(d)-listed as mercury impaired as of 2006, and 12 discharge to small waterways that, although not 303(d)-listed, drain directly to the Delta/Yolo Bypass. Table 15 summarizes the number of facilities that received the Order, categorized by discharger type and geographical region.

Effluent methylmercury data were submitted by 111 facilities as a result of the 13267 Order monitoring requirements. Although not required by the Order, thirty-six of those facilities also submitted influent methylmercury data. In addition, the Sacramento Regional County Sanitation District submitted influent and effluent methylmercury concentration data for a six-year period (December 2000 – March 2007). Central Valley Water Board staff compiled influent and effluent inorganic mercury concentration data available in SRCSD monitoring reports. The abundance of inorganic mercury and methylmercury data for the SRCSD Sacramento River WWTP influent and effluent allowed for more analysis of the SRCSD data. Figures 1, 2 and 3 illustrate the locations of the Central Valley facilities that submitted methylmercury data and Table 16 provides the map codes, receiving water information, approximate discharge volumes and facility types discussed in this report.

Tables G.3a and G.3b in Appendix G of the Delta methylmercury TMDL report summarize the number of effluent methylmercury samples collected by each facility, along with their average, minimum and maximum methylmercury concentrations. Tables in the Delta methylmercury TMDL report appendix provide average concentrations only for discharges to surface water. The graphs and calculations in this

[3] The "Delta Source Region" is a geographic area that includes the Delta and the watershed areas upstream that drain into the Delta but are downstream of major dams.

report incorporate all available data, including samples collected when facilities did not discharge to surface water. Of the approximately 700 effluent methylmercury samples collected, nine samples were taken from reclaimed effluent that was not discharged to surface water.

Available influent and effluent data are summarized by discharger type in the following sections. Summaries of effluent and influent methylmercury data for each NPDES facility are presented in Appendix B, Tables B.1 through B.4, at the end of this report.

4.1 Non-Municipal Discharges

Section 4.1 is divided into six subsections that describe non-municipal discharges:

1. Aggregate;
2. Aquaculture, power generation and heating/cooling;
3. Paper, pulp and saw mills;
4. Groundwater remediation;
5. Drinking water treatment; and
6. Food processing, manufacturing, and other non-municipal discharges.

A summary of the effluent methylmercury concentration data categorized by discharger type for the non-municipal NPDES facilities is provided in Table 17.

4.1.1 Aggregate

Discharge from aggregate plants, which process rock and gravel from quarries, is typically storm water after it is settled in sedimentation basins. These facilities were a small source of methylmercury with an average effluent concentration of 0.026 ng/l (Table 17). Five aggregate facilities submitted discharge methylmercury concentration data; one of the facilities is no longer active. Six of the eight samples collected by the active aggregate plants had methylmercury concentrations less than the method detection limit, and the other two samples had concentrations of 0.062 and 0.081 ng/l. Discharges from aggregate plants comprise about 2% of NPDES discharges (by volume) to the Delta source region.

The Oakwood Lake Subdivision Mining Reclamation NPDES permit (CA0082783; formerly known as the Brown Sand, Inc., Manteca Aggregate Sand Plant) allows for the discharge of water from Oakwood Lake to the San Joaquin River for flood control. Oakwood Lake is a former excavation pit filled primarily by groundwater. The results from discharge sampling in August and November 2004, nondetect (<0.02 ng/l) and 0.043 ng/l, respectively, are comparable to results for groundwater remediation plant discharges (Section 4.1.4). Furthermore, these effluent values are substantially lower

than the monthly average methylmercury concentrations observed in the adjacent San Joaquin River at Vernalis during August and November (0.167 and 0.130 ng/l, respectively; Wood *et al.*, 2010b).

4.1.2 Aquaculture, Power Generation & Heating/Cooling

Aquaculture, power generation, and heating/cooling facilities typically use ambient surface water, domestic water or groundwater for hatchery flow-through water or cooling water. Wastewater from these types of facilities may be untreated, filtered to remove solids and/or metals, or clarified in sedimentation basins prior to discharge. The combined discharge volume from all of these facility categories is about 50% of the total discharged by NPDES facilities to the Delta source region (Table 14).

Aquaculture, power generation and heating/cooling facilities had average effluent methylmercury concentrations of 0.041 ng/L, 0.061 ng/L and 0.11 ng/L, respectively (Table 17). The intake water of many of these facilities is taken from the same water body that the effluent is discharged to; therefore, a comparison of intake and effluent concentrations is necessary to determine whether a facility is a net source or sink of methylmercury.

Ten of the twenty-four facilities that submitted methylmercury data collected paired intake/outfall samples (Table 18). The power and heating/cooling facilities did not appear to be a source of methylmercury to the Delta. However, staff was unable to do statistical analyses of the paired influent-effluent samples of these facilities because sample sizes were too small for all facilities except for Mirant Delta CCPP (CA0004863), a power generation facility. Furthermore, many of these facilities had influent and effluent samples that were below the detection limit, making it impossible to statistically compare those paired samples. Methylmercury concentrations of outfalls 1 and 2 from Mirant Delta CCPP were not significantly different than intake 2 when compared individually (Outfall 1 vs. Intake 2: $p=0.26$; Outfall 2 vs. Intake 2: $p=0.37$, paired t-test). Therefore, outfalls 1 and 2 were neither significant sources nor sinks of methylmercury. More data is necessary to determine if the other power and heating/cooling facilities are methylmercury sources or sinks.

Effluent methylmercury concentrations of the aquaculture facilities were not significantly different than the paired influent concentrations ($p=0.21$, paired t-test). Even though the effluent concentrations typically exceeded intake concentrations (see Table 18), aquaculture facilities were neither a source nor sink of methylmercury. This comparison is based upon five paired influent-effluent samples from three facilities; therefore, more paired data is necessary to determine if aquaculture facilities are net sources or sinks. Almost all the aquaculture facilities had average effluent methylmercury concentrations equal to or less than 0.05 ng/l.

Until recently, the SMUD Rancho Seco Nuclear Generating Station (CA0004758) discharged a combination of treated liquid radioactive wastewater, secondary treated domestic wastewater, stormwater and irrigation runoff. It is the only facility in the power generation/ domestic WWTP category and was a small source of methylmercury. Methylmercury concentrations in the combined effluent ranged from nondetect (<0.025 ng/l) to 0.104 ng/l with an average of 0.040 ng/l.

4.1.3 Paper, Pulp & Saw Mills

Paper, pulp and saw mills discharge a combination of process wastewater and storm water after it is typically clarified in settling basins. These facilities were a source of methylmercury with an average effluent concentration of 0.117 ng/l (Table 17). However, 15 of the 21 effluent samples collected at these facilities were less than 0.10 ng/l. Paper, pulp and saw mills account for about 0.4% of the volume discharged by NPDES facilities to the Delta source region.

Five of the 12 effluent samples collected at the Pactiv Molded pulp mill (CA0004821) had methylmercury concentrations less than the method detection limit, and the other seven samples were between the detection limit and 0.085 ng/l. Eight of the nine samples collected at the two other mills had concentrations between the detection limit and 0.18 ng/l. The SPI Shasta Lake saw mill (CA0081400) had the highest effluent methylmercury concentration of 1.19 ng/l, collected from “Discharge 002” on 30 December 2004. The concentration of the other effluent sample collected from “Discharge 002” on 23 March 2005 at this facility was 0.023 ng/l. Discharge 002 is from a stormwater retention pond, and rainfall occurred on both sample dates and on previous days; it is conceivable that a “first flush” effect could be the cause of the highly variable results.

4.1.4 Groundwater Remediation

Groundwater remediation facilities extract contaminated groundwater for treatment prior to discharge to surface waters. These facilities had very low levels of methylmercury in their discharge. Nineteen of the 20 effluent samples collected by four facilities had methylmercury concentrations less than the method detection limit, and one sample was just slightly above the detection limit (0.033 ng/l). One plant collected nine influent samples, all of which had methylmercury concentrations less than the detection limit. Groundwater remediation plants account for about 1.4% of the volume discharged by PDES facilities to the Delta source region.

4.1.5 Drinking Water Treatment

Drinking water treatment plants account for about 0.1% of the volume discharged by NPDES facilities to the Delta source region. Drinking water treatment plants typically

discharge settled filter backwash water from their treatment process to surface waters. Six drinking water treatment facilities submitted effluent methylmercury concentration data and two of those submitted influent data. These facilities had an average effluent concentration of 0.033 ng/l (Table 17). Five of the facilities had effluent samples with methylmercury concentrations ranging from below the detection limit to 0.043 ng/l. One of these facilities collected an intake sample with a methylmercury concentration of 0.084 ng/l. The other facility had two effluent samples with methylmercury concentrations measuring 0.045 ng/l and 0.066 ng/l, and two influent samples with concentrations measuring less than the detection limit (0.02 ng/l) and 0.033 ng/l.

4.1.6 Food processing, Manufacturing, and other Non-Municipal Discharges

Food processing, manufacturing, and publishing facilities were not a substantial source of methylmercury. Fifteen of the 20 effluent samples collected by facilities in these categories had methylmercury concentrations less than the method detection limit, and the other five samples had concentrations between the detection limit and calibration standard (0.05 ng/l). One of the manufacturing facilities collected 12 influent samples. Eleven of these samples had methylmercury concentrations less than the detection limit, and one was just above the detection limit.

The one laboratory and one mine facility that submitted data were both small sources of methylmercury. The three samples collected by the laboratory facility had methylmercury concentrations between 0.038 ng/l and 0.082 ng/l. The four samples collected by the mine ranged from 0.025 ng/l to 0.091 ng/l. Permitted discharges from food processing, mining, publishing, and laboratory facilities comprise about 0.3% of the total NPDES discharge volume to the Delta source region. The two manufacturing plants in the Delta source region have since ceased discharge to surface waters.

4.2 Municipal WWTPs

More information is available for municipal WWTPs than for other types of NPDES facility discharges, so staff was able to conduct a more extensive data analysis for WWTPs. Municipal WWTPs contribute about 44% of the total discharge volume (see Table 14) and about 99% of methylmercury loading contributed to the Delta source region by NPDES facilities (see Chapter 5 and Table 36). While the loads from all WWTPs may be a small fraction of the total and methylmercury loads from tributary and Delta sources (see Chapter 5 and Tables 35, 36 and 37), some municipal WWTPs may contribute substantial methylmercury loads to individual water bodies. For example, a six-year comparison of the SRCSD Sacramento River WWTP effluent methylmercury loads as a percentage of its receiving water loads was as high as 30 to 43% during the warm seasons of 2001 and 2002 and less than 1% during the wet seasons of 2005 and 2006 (Figure 4; Bosworth, 2008), ranging from 4.2% to 17% on an annual basis.

Between October 2002 and October 2006 most of the loading was less than 10% during the winter through summer seasons. For some receiving waters, reducing municipal WWTP methylmercury discharges, along with reductions from other point and nonpoint sources, may be an important component in reducing methylmercury levels in Delta water.

Sixty-one municipal WWTPs submitted effluent methylmercury concentration data representing 63 discharges (two facilities had two discharge locations). Twenty-three treatment plants also submitted influent methylmercury data. In addition, inorganic mercury influent and effluent data are available for 9 and 29 discharges, respectively. Hence, Section 4.2 is divided into subsections describing the different types of concentration data and data comparisons:

1. Effluent methylmercury;
2. Influent methylmercury;
3. Effluent inorganic mercury;
4. Influent inorganic mercury;
5. Ratio between effluent methylmercury and influent methylmercury;
6. Ratio between effluent methylmercury and effluent inorganic mercury;
7. Ratio between effluent methylmercury and influent inorganic mercury; and
8. Ratio between effluent inorganic mercury and influent inorganic mercury.

To begin the process of evaluating methylmercury discharges from municipal WWTPs, Board staff conducted a preliminary evaluation of municipal treatment process information available in NPDES permits and project files. Table 20 provides treatment process information with the WWTPs sorted by average effluent methylmercury concentration. Using this treatment process information, staff grouped the Central Valley WWTPs into mutually exclusive categories based on the maximum level of wastewater treatment that the facilities were using in 2005, including the secondary, tertiary and disinfection treatment types (Table 21). A description of the treatment categories is provided in Table 22 and descriptive statistics for these categories are provided in Table 23. For calculations involving inorganic mercury and methylmercury concentration results that were less than the method detection limit (MDL), one half of the MDL was used for those results.

Staff attempted to identify obvious differences and seasonal trends in influent and effluent data between facilities and evaluated those differences in terms of the treatment categories. Identifying the reasons why some WWTPs discharge effluent with higher methylmercury concentrations than others, and why some facilities have seasonal or other treatment-related variability in their methylmercury discharges, could be critical components to the development of methylmercury controls.

4.2.1 Effluent Methylmercury

Municipal WWTPs had the most variability in effluent methylmercury concentrations of any of the NPDES discharger categories evaluated. Individual effluent methylmercury concentrations ranged from nondetect (<0.02 ng/l at 31 WWTPs) to 4 ng/L at the Colusa WWTP, a 200-fold difference. As illustrated by Figure 5, 20 (33%) of the WWTPs had average effluent methylmercury concentrations less than 0.05 ng/l, and 13 (21%) plants had average concentrations less than 0.03 ng/l. In contrast, 18 (30%) WWTPs had average effluent methylmercury concentrations greater than 0.2 ng/l, and 7 of these averaged between 1 and 2.9 ng/l. The highest average effluent methylmercury concentration (2.86 ng/l) observed at a facility was nearly 150 times that of the lowest average concentrations (e.g., facilities with effluent concentrations approaching or less than the detection limit). As shown in Table 1, the variability in the methylmercury concentrations observed in effluent from different municipal WWTPs in the Central Valley is comparable to WWTP effluent concentrations observed elsewhere.

Municipal WWTPs with higher average effluent methylmercury concentrations generally had higher variability, as indicated by a positive relationship ($R^2 = 0.7167$, $p<0.0001$) between the WWTPs' average methylmercury concentrations and corresponding standard deviations (Figure 6).

Seasonal variability was observed in effluent methylmercury concentrations at several municipal WWTPs. Anderson, Cottonwood, Davis, Grass Valley, Lincoln, Oroville, Placer Co. SMD #1, Redding Clear Creek and SRCSD Sacramento River WWTPs had higher effluent methylmercury concentrations in the warm season (e.g., May through November) than the cool season (see Figures 7 and 8). The exception was the Stockton WWTP, which had higher concentrations in the cool season. No obvious relationship between seasonality and treatment processes exists.

The SRCSD Sacramento River WWTP has a six-year methylmercury monitoring record for both the influent and effluent. Monthly averages of all the effluent methylmercury concentrations collected during the six-year period were higher during the warm season than during cold weather (Figure 8). However, the most recent data collected during WY2005-2007 show much less seasonal variability and lower methylmercury concentrations during warm months (May – November) than in earlier years ($p<0.0001$ for both the non-parametric Mann-Whitney U test and the parametric two sample t-test). Overall, SRCSD effluent methylmercury concentrations showed a marked decrease from WY2001 to 2007 (Figure 9).

Staff used statistical tests to determine if significant differences in effluent methylmercury concentrations exist between the treatment categories. Descriptive statistics and normality tests indicate that the treatment categories do not meet the assumptions of parametric hypothesis tests, including homoscedasticity (constant

variance) among all groups and data normality (Table 23). Differences in effluent methylmercury concentrations between the treatment categories were analyzed with non-parametric statistics as transformations could not be found to produce homoscedasticity and data normality among the all of the categories. The "Statistica" software was employed for all the statistical analyses.[4]

Statistically significant differences in effluent methylmercury concentrations exist among the treatment categories ($p<0.0001$, Kruskal-Wallis test). A pair-wise multiple comparison test was conducted to determine which treatment categories had higher concentrations. The two-sided significance levels (p-values) for each treatment category are presented in Table 24.

Facilities that use treatment pond systems as part of their treatment process had the highest effluent methylmercury concentrations (Figures 10 and 11; Table 23). The "Pond + Chlorination/Dechlorination (C/D)" and "Pond + Filtration + C/D" treatment categories had median effluent methylmercury concentrations of 0.52 ng/l and 0.81 ng/l, respectively. Conversely, facilities that have some combination of nitrification/denitrification (N/D), filtration, and ultraviolet (UV) disinfection generally had lower effluent methylmercury concentrations. The "N/D + Filtration + C/D", "Secondary w/ N/D + UV", "N/D + Filtration + UV", "Filtration + UV", "Secondary w N/D + C/D" and "Filtration + C/D" categories had median effluent methylmercury concentrations of 0.06 ng/l or less (Table 23).

These observed trends are confirmed by the multiple comparison p-values for the treatment categories. The "Pond + C/D" and "Pond + Filtration + C/D" categories had significantly higher effluent methylmercury concentrations than the "N/D + Filtration + C/D", "Secondary w/ N/D + UV", "N/D + Filtration + UV", "Filtration + UV", "Secondary w/ N/D + C/D" and "Filtration + C/D" categories ($p<0.00001$; Table 24). In addition, the "Secondary + C/D" category had significantly higher concentrations than every other category ($p<0.01$), excluding the "Pond + C/D" and "Pond + Filtration + C/D" categories (Table 24). Other statistically significant differences in effluent methylmercury concentrations include: the "Pond + C/D" category had higher values than the "Secondary + C/D" category, and the "N/D + Filtration + C/D" category had lower values than the "Secondary w/ N/D + C/D" and "Filtration + C/D" categories.

As indicated by Figure 10, two WWTPs had different effluent methylmercury concentrations than other WWTPs in the same treatment category:

- The Modesto WWTP had lower effluent methylmercury concentrations than other WWTPs in the "Pond + C/D" category ($p<0.0001$ for both the Mann-Whitney U test and the two sample t-test);

[4] Statistica StatSoft, http:// www.statsoft.com

- The Rio Alto WWTP had higher effluent methylmercury concentrations than other WWTPs in the “Filtration + C/D” category. Since only two effluent samples were collected at this WWTP, more data is needed to determine if these concentrations are representative of this facility’s effluent.

These differences suggest that other unique processes are acting at these two facilities that significantly modify methylmercury production or degradation. Staff’s review of the other treatment processes and data for these facilities (e.g., Tables 20 and 21, Figure 7) gave no straightforward reasons for the differences. The Rio Alto WWTP had more variability (i.e., coefficient of variation) than all but one of the 17 WWTPs in the "Filtration +C/D" category. The Modesto WWTP had the lowest average effluent methylmercury concentration and coefficient of variation of all of the 11 WWTPs in the “Pond + C/D” category. It could be helpful to obtain more information about conditions during each of the sampling events for these WWTPs (e.g., variations in treatment methods and differences in nitrate concentrations and temperature) and, in the future, to sample both influent and effluent to assess whether the variability in effluent is due to influent variability or treatment variability.

Nitrification/denitrification, filtration, ultraviolet disinfection or a combination of these treatments may play a role in decreasing effluent methylmercury concentrations. The “N/D + Filtration + C/D” category had significantly lower effluent methylmercury concentrations than the “Secondary w/ N/D + C/D” and “Filtration + C/D” categories (Table 24). This suggests that both filtration and nitrification/denitrification treatment processes may have been responsible for the lower concentrations discharged by the facilities in the “N/D + Filtration + C/D” category.

During the nitrification process, aerobic bacteria convert ammonia to nitrate with the assistance of oxygen (Metcalf and Eddy, Inc., 1972). The denitrification process involves anoxic bacteria converting nitrate to nitrogen gas with the help of a carbon source such as methanol (Metcalf and Eddy, Inc., 1972). The denitrification bacteria potentially could assist in the demethylation of methylmercury to inorganic mercury, because the methyl group is the best carbon source for the conversion of nitrate to nitrogen gas (Pirondini, 2008a). This potential methylmercury demethylation could occur in a fully-nitrified wastewater (low ammonia), but likely not in a partially-nitrified or non-nitrified wastewater (high ammonia) (Pirondini, 2008a). Additional analysis that directly evaluates effluent ammonia/nitrate/nitrite levels and effluent methylmercury concentrations needs to take place.

The “Filtration + C/D” and “Secondary + C/D” treatment categories both contained numerous WWTPs with a variety of secondary treatment types. Staff assigned the WWTPs in each of these groups into three mutually exclusive subcategories based upon their secondary treatment (Table 25). The three subcategories were “Activated Sludge” (includes conventional, pure oxygen and extended aeration activated sludge,

oxidation ditch and sequencing batch reactor treatments), “Activated Sludge + Trickling Filter” and “Fixed Media” (includes trickling filter and rotating biological contactor treatments). Descriptive statistics and normality tests indicate that the subcategories within each treatment grouping do not meet the assumptions of parametric hypothesis tests (Table 26). Differences in effluent methylmercury concentrations between the treatment subcategories were analyzed with non-parametric statistics as transformations could not be found to produce homoscedasticity and data normality among the all of the categories.

Within the “Secondary + C/D” category, no significant differences in effluent methylmercury concentrations exist between the three subcategories ($p=0.07$, Kruskal-Wallis test). However, within the “Filtration + C/D” category, significant differences exist between the subcategories ($p<0.01$, Kruskal-Wallis test). A pair-wise multiple comparison test indicated that the “Activated Sludge” subcategory had lower effluent methylmercury concentrations than the “Fixed Media” subcategory ($p<0.01$; Table 27). Descriptive statistics for the subcategories within each treatment category are presented in Table 26.

Each subcategory within the “Filtration + C/D” category had lower average and median effluent methylmercury concentrations than the same subcategory within the “Secondary + C/D” category (Table 25). These differences are statistically significant as shown by the two-sided significance levels (p-values) in Table 28. This indicates that the filtration treatment process may have assisted in the reduction of methylmercury in the effluent of these facilities.

4.2.2 Influent Methylmercury

A seasonal pattern was observed in influent methylmercury concentrations at a few municipal WWTPs. Several plants appeared to experience a decrease in influent methylmercury concentrations during cool weather months (Chico, Deer Creek and El Dorado Hills WWTPs); while some showed a sharp increase in the spring (Williams and Woodland WWTPs) or the summer (Rio Vista and UC Davis WWTPs) (see Figure 13). The approximately six-year influent methylmercury monitoring record for the SRCSD Sacramento River facility also showed an increase in average influent concentrations during the summer months (Figure 14). As for effluent methylmercury, there appeared to be a decreasing trend in influent methylmercury concentrations at the SRCSD Sacramento River facility between WY2001 to WY2007 (Figure 9).

Average influent methylmercury concentrations ranged from 0.068 at Mariposa WWTP to 14.6 ng/l at Maxwell WWTP, a 215-fold difference (Figure 12). Of the 23 municipal WWTPs that collected influent methylmercury data, three had average influent methylmercury concentrations less than 1 ng/l, ten had average concentrations between 1 ng/l and 2 ng/l, and two had average concentrations greater than 7 ng/l.

4.2.3 Effluent Inorganic Mercury

Effluent inorganic mercury concentrations ranged from non-detect (less than 0.2 ng/l) at the Modesto WWTP to 53.1 ng/l at the Woodland WWTP, which is about a 260-fold difference (Figure 15). The high value observed at the Woodland WWTP was an anomaly when compared to the remainder of the Woodland WWTP data. Of the 28 WWTPs where effluent inorganic mercury data were collected, 10 had average effluent inorganic mercury concentrations less than 3 ng/l, 11 had average concentrations between 3 ng/l and 7 ng/l, and two had average concentrations greater than 10 ng/l. The highest average effluent inorganic mercury concentration (22 ng/l) observed at a WWTP was about 44 times that of the lowest average concentration (0.5 ng/l; Figure 15).

Several WWTPs had higher effluent inorganic mercury concentrations during the winter (Davis [Discharge 1], Manteca, Placer County SMD #1 and Stockton WWTPs) or spring (Redding Stillwater WWTP) (see Figure 16). No obvious relationship between seasonality and treatment processes seemed to exist. The effluent inorganic mercury monitoring record for the SRCSD Sacramento River facility showed relatively constant monthly averages (between 5 ng/l and 7 ng/l) with no apparent seasonal trend (Figure 17). However, effluent inorganic mercury data collected from December 2000 to March 2007 showed an obvious decreasing trend, particularly after 2004 (Figure 18). Furthermore, the effluent inorganic mercury concentrations from 2005 to 2007 had much less variability than the prior years.

4.2.4 Influent Inorganic Mercury

Of the 61 municipal WWTPs that monitored effluent methylmercury, nine WWTPs monitored influent inorganic mercury. Influent inorganic mercury concentrations ranged from 29.0 ng/l at Roseville Pleasant Grove WWTP to 6,100 ng/l at SRCSD Sacramento River WWTP, which is about a 210-fold difference (Figure 19). Two of the nine facilities that collected data had average influent inorganic mercury concentrations less than 100 ng/l, four facilities were between 100 ng/l and 300 ng/l, and 3 facilities had average influent concentrations greater than 300 ng/l. The highest average influent inorganic mercury (2,100 ng/l) observed at a municipal WWTP was about 60 times that of the lowest average concentration (35.5 ng/l).

Because of the limited data set, there was not enough information to discern any seasonal patterns. The Lodi White Slough WWTP had higher influent inorganic mercury concentrations in the fall and winter, the Roseville Pleasant Grove WWTP had higher concentrations in the summer, and two WWTPs (Roseville Dry Creek and Woodland WWTPs) had no discernable pattern (Figure 20).

Board staff compiled influent inorganic mercury data for the SRCSD Sacramento River WWTP collected from December 2000 – December 2004 that were available in a variety of monitoring reports and special study documents in the permit files (SRCSD, 2004; SRCSD, 2005). The influent inorganic mercury data for this four-year period had no interannual (Figure 21) or seasonal trends (Figure 22). The monthly averages for the SRCSD Sacramento River WWTP varied between 120 ng/l and 300 ng/l, with the exception for two months, January and March (Figure 22). These were observably higher than other months as a result of two anomalously high values. One of these two values was collected on 6 January 2004 (6,100 ng/l) and the other on 11 March 2004 (3,400 ng/l). Three other influent samples collected during the four-year period had inorganic mercury concentrations greater than 1,000 ng/l, one each in 2001, 2002 and 2004.

4.2.5 Ratio between Effluent Methylmercury and Influent Methylmercury

The ratios between paired effluent and influent methylmercury concentrations were calculated to determine the methylmercury removal efficiencies of the municipal WWTPs. A percent value less than 100% for a given municipal WWTP indicates that its treatment processes caused a net reduction in methylmercury; a percent value greater than 100% indicates that the plant was a net methylmercury source. Average ratios ranged from 1.1% at El Dorado Hills WWTP (Discharge 2) to 803% at Mariposa WWTP. Of the 23 WWTPs where both effluent and influent methylmercury data were collected, 14 had average effluent:influent methylmercury ratios less than or equal to 10%, and 11 of those had average ratios less than or equal to 5% (Figure 23). In contrast, five WWTPs had average ratios greater than 30%. Municipal WWTPs in the "Secondary + C/D" and "Pond + C/D" treatment categories had lower methylmercury removal efficiencies indicated by higher effluent:influent ratios than WWTPs in all other treatment categories (Figure 24; Table 29; $p<0.04$, Kruskal-Wallis test).

Three facilities (Colusa, Mariposa and SRCSD Walnut Grove WWTPs) had average ratios greater than 100%, indicating that these facilities were net producers of methylmercury. As seen in Figure 23, two of these average effluent:influent methylmercury ratios (254% for Colusa and 803% for Mariposa) were much higher than the average ratios of the remainder of the facilities. The closest value to these is from the SRCSD Walnut Grove WWTP, which had an average ratio of 101%. The Colusa and SRCSD Walnut Grove WWTPs are both in the "Pond + C/D" treatment category, while the Mariposa WWTP is in the "Secondary + C/D" category. These average ratios are based upon one or two paired influent and effluent samples collected at the WWTP. More data is needed to determine if these removal efficiencies are representative of these facilities.

Several facilities exhibited seasonal variability in methylmercury removal (Figures 25 and 26). Lower removal efficiencies indicated by higher ratios occurred during the

summer or fall for some facilities (Grass Valley, Rio Vista, Roseville Dry Creek, Roseville Pleasant Grove and SRCSD Sacramento River WWTPs), and during winter for others (Chico, Deer Creek and El Dorado Hills [Discharge 1] WWTPs). No relationship was apparent between seasonal variability and the type of treatment process.

The methylmercury removal efficiency for SRCSD Sacramento River WWTP's six-year record showed an increasing trend indicated by a decrease in its ratios (Figure 27). These ratios differed temporally, in that the WY2001-2004 period showed much more seasonal variability with higher ratios in the warm season (May – November) than did the ratios for the WY2005-2007 period (Figure 26; $p<0.001$ for both the Mann-Whitney U test and the two sample t-test). This trend between earlier and later time periods was similarly seen in the effluent methylmercury concentrations for SRCSD Sacramento River WWTP and may be the reason for the observed trend in the ratios (Figure 8).

As mentioned in sections 4.2.1 and 4.2.2, decreasing trends were observed both in influent and effluent methylmercury concentrations for the SRCSD Sacramento River WWTP between WY2001 and WY2007 (Figure 9). The decrease in effluent methylmercury concentrations could be partially due to the concurrent decrease in influent concentrations; however, the regression for effluent methylmercury has a steeper decreasing slope (-0.0001) than does the influent line (-0.00008) indicating an improved methylmercury removal efficiency since WY2001 (Figure 9). Furthermore, Figure 27 shows an increasing trend in methylmercury removal efficiency between WY2001 and WY2007.

Staff reviewed scatter plots of paired influent and effluent methylmercury concentrations to determine whether there was a relationship between the two. The paired samples may not represent the same parcels of water due to in-plant residence time. The scatter plot of all paired data from all WWTPs excluding SRCSD Sacramento River WWTP showed a significant positive relationship ($R^2 = 0.1347$, $p<0.0001$; Figure 28a). The scatter plot including data from SRCSD Sacramento River WWTP also showed a statistically significant positive relationship ($R^2 = 0.0715$, $p<0.0001$; Figure 28b). Staff analyzed scatter plots with and without data from SRCSD Sacramento River WWTP because the number of paired data points from the SRCSD Sacramento River WWTP (n=107) was relatively high compared to other WWTPs (n=1 to 16). These significant relationships indicate that reductions in methylmercury in the effluent were in part due to lower influent concentrations. However, only 7-13% of the variability in effluent methylmercury concentrations was explained by influent concentrations, indicating that effluent concentrations were substantially affected by other factors. Influent methylmercury concentrations alone were not a good predictor of effluent concentrations.

Of the 23 WWTPs that submitted both influent and effluent methylmercury concentration data, 10 WWTPs submitted paired data for five or more sampling events (Figures 29 and 30). When analyzed individually, none of these facilities had significant relationships between influent and effluent methylmercury concentrations except Lodi WWTP ($R^2 = 0.404$, $p<0.03$), UC Davis WWTP ($R^2 = 0.388$, $p<0.04$) and SRCSD Sacramento River WWTP ($R^2 = 0.174$, $p<0.0001$; see Table 30 for R^2 and p-values for each WWTP). All three facilities exhibited positive relationships; however, the significant positive relationship for Lodi WWTP appeared to be driven by one paired data point collected on 13 April 2005 (influent 2.74 ng/l, effluent 1.24 ng/l). When this point was removed, no significant relationship exists ($R^2 = 0.090$, $p>0.05$). Influent versus effluent methylmercury scatter plots for SRCSD Sacramento River WWTP indicated a significant positive relationship for the paired data collected during the cool season (December through April; $R^2 = 0.262$, $p<0.001$), but not during the warm season (May through November; $R^2 = 0.015$, $p>0.05$; Figure 30). Again, only about 26% of the variability in cool season effluent methylmercury concentrations was explained by influent concentrations, which indicates that effluent methylmercury concentrations were affected by other factors as well.

4.2.6 Ratio between Effluent Methylmercury and Effluent Inorganic Mercury

The ratios between paired effluent methylmercury and effluent inorganic mercury concentrations were calculated to estimate the percentage of inorganic mercury as methylmercury in the effluent and to see if differences exist between treatment types. Average ratios ranged from 0.60% at Discovery Bay WWTP to 28% at Nevada County Sanitation District #2 Lake of the Pines WWTP. Of the 28 WWTPs where both methylmercury and inorganic mercury were analyzed in the effluent, 24 had average effluent methylmercury:inorganic mercury ratios less than or equal to 10%, and 19 of those had average ratios less than or equal to 5% (Figure 31). Only four discharges had average ratios greater than 10%. The average effluent methylmercury:inorganic mercury ratio for SRCSD Sacramento River WWTP was 10%; the ratio appeared to increase slightly from WY2001 to WY2007 (Figure 32).

Municipal WWTPs in the “Pond + Filtration + C/D” maximum treatment category had higher effluent methylmercury:inorganic mercury ratios than WWTPs in all other treatment categories except for the “Pond + C/D” category (Figure 33; Table 31; $p<0.03$, Kruskal-Wallis test). In addition, the “Pond + C/D” and “Secondary + C/D” categories had higher ratios than the “Secondary w/ N/D + UV”, “N/D + Filtration + C/D” and “Filtration + UV” categories ($p<0.01$, Kruskal-Wallis test).

Five municipal WWTPs appeared to have well-defined seasonal variability in their effluent methylmercury:inorganic mercury ratios (Figures 34 and 35). The following WWTPs appeared to experience an increase in their ratio in the spring and/or summer: Davis (Discharges 1 and 2), Manteca, Placer County SMD #1, SRCSD Sacramento

River, and Stockton. No discernable relationship between the seasonal variability of the ratios and the types of treatment processes were apparent.

Staff reviewed scatter plots to determine whether there was a relationship between effluent methylmercury and inorganic mercury concentrations. The scatter plot of all paired data from all WWTPs excluding SRCSD Sacramento River WWTP showed a significant positive relationship ($R^2 = 0.0431$, $p<0.01$; Figure 36a). The anomalous value collected at Woodland WWTP on 9 December 2004 (THg: 53.1 ng/l, MeHg: below detection limit of 0.025 ng/l) appeared to strongly influence the trend-line. The scatter plot after removing the anomalous paired data-point continued to indicate a statistically significant positive relationship ($R^2 = 0.0779$, $p<0.0001$). The scatter plots including data from SRCSD Sacramento River WWTP also showed significant positive relationships with ($R^2 = 0.0704$, $p<0.0001$) and without the Woodland WWTP outlier ($R^2 = 0.1155$, $p<0.0001$; Figure 36b). Only 4-12% of the variability in effluent methylmercury concentrations was explained by effluent total mercury concentrations for the different WWTPs, indicating that effluent concentrations were substantially affected by other factors.

Of the 28 WWTPs that submitted effluent methylmercury and inorganic mercury concentration data for a total of 29 discharges, 20 WWTPs submitted paired data for five or more sampling events (Figures 37 and 38). Some WWTPs appeared to have positive relationships between effluent methylmercury and inorganic mercury, however only four facilities (Discovery Bay, Stockton, SRCSD Sacramento River and Davis WWTPs) had a statistically significant relationship (Discovery Bay : $R^2 = 0.551$, $p<0.03$; Stockton: $R^2 = 0.67$, $p<0.01$; SRCSD: $R^2 = 0.0775$, $p<0.01$; Davis: $R^2 = 0.4445$, $p<0.02$; Table 32). Seasonal scatter plots for SRCSD Sacramento River WWTP did not indicate significant positive relationships for all of the paired data collected from WY2001 to WY2007 for both the warm (May through November; $R^2 = 0.061$, $p>0.05$) and cool (December through April; $R^2 = 0.071$, $p>0.05$) seasons (Figure 38).

4.2.7 Ratio between Effluent Methylmercury and Influent Inorganic Mercury

The ratios between paired effluent methylmercury and influent inorganic mercury concentrations were calculated to determine if a relationship existed between influent inorganic mercury and effluent methylmercury, and to explore how the ratios may relate to treatment processes. Ultimately, it would be very useful to know whether reducing influent inorganic mercury concentrations (e.g., by implementing mercury source minimization measures[5]) would result in reductions in effluent methylmercury, and if so, by how much.

[5] For example, residential drop-off programs for mercury-containing products and best management practices for hospitals, dentists, other medical facilities, laboratories, and pottery studios.

Average ratios ranged from 0.0005% at the Lincoln WWTP to 1.85% at the Davis WWTP (Discharge 1) (Figure 39). The average effluent methylmercury:influent inorganic mercury ratio for SRCSD Sacramento River WWTP was 0.45%; the ratio did not appear to change from December 2000 to December 2004 (Figure 40). Two of the five facilities with more than six paired samples (Lodi White Slough and SRCSD Sacramento River WWTPs) had an apparent seasonal pattern, with an increase in effluent methylmercury:influent inorganic mercury ratio in the summer (see Figures 41 and 42).

Staff reviewed scatter plots to determine whether there was any relationship between effluent methylmercury and influent inorganic mercury concentrations. The scatter plots of all paired data for all WWTPs with and without the SRCSD Sacramento River WWTP data showed no relationship (with SRCSD: $R^2 = 0.0026$, $p>0.05$, Figure 43a; without SRCSD: $R^2 = 0.0206$, $p>0.05$, Figure 43b). The relationship between effluent methylmercury and influent inorganic mercury loads may present a different conclusion, but was not assessed in this report.

Of the nine municipal WWTPs that submitted effluent methylmercury and influent inorganic mercury concentration data, five facilities submitted paired data for five or more sampling events. No relationships between effluent methylmercury and influent inorganic mercury were observed for any of these five facilities individually (Figures 44 and 45a; Table 33). Scatter plots for SRCSD Sacramento River WWTP showed no relationship for data collected from December 2000 to December 2004 (all data: $R^2 = 0.0017$, $p>0.05$; warm season: $R^2 = 0.0311$, $p>0.05$; cool season: $R^2 = 0.0182$, $p>0.05$; Figure 45a). After removing the paired data that included the anomalously high value collected on 6 January 2004 (6,100 ng/l) at the SRCSD Sacramento River WWTP, the scatter plots still indicated no significant relationships (all data: $R^2 = 0.0045$, $p>0.05$; warm season: $R^2 = 0.0311$, $p>0.05$; cool season: $R^2 = 0.0044$, $p>0.05$; Figure 45b).

The SRCSD District Engineer presented a chart of annual influent inorganic mercury and effluent methylmercury loads for 2001 through 2007 during testimony for the April 2008 hearing for the Delta mercury control program (see Figure 46). The SRCSD District Engineer indicated that the WWTP's effluent inorganic mercury and methylmercury decreased as a result of influent inorganic mercury decreases associated with the initiation of their "Be Mercury Free" source control program. This additional influent inorganic mercury data from 2005 to 2007 was not available at the time this report was written.

4.2.8 Ratio between Effluent Inorganic Mercury and Influent Inorganic Mercury

The ratios between paired effluent and influent inorganic mercury concentrations were calculated to determine by how much the municipal WWTPs reduced inorganic mercury- the lower the ratio, the higher the removal efficiency. Average ratios ranged

from 0.6% at the Woodland WWTP to 27% at the Merced WWTP (Figure 47). Of the eight WWTPs that submitted paired influent and effluent inorganic mercury data, five of the facilities had average effluent:influent inorganic mercury ratios less than or equal to 5%, and two had average ratios greater than 15%. No discernable relationship between removal efficiency and the types of treatment processes were observed.

Two of the five facilities with six or more paired samples had an apparent seasonal pattern (Figures 48 and 49). The Lodi White Slough WWTP appeared to have a lower inorganic mercury removal efficiency during the summer, while the Roseville Dry Creek appeared to have a lower removal efficiency during the winter-spring. The ratios for the SRCSD Sacramento River WWTP showed no seasonal patterns (Figure 49).

Scatter plots of all paired data for all WWTPs with and without the SRCSD Sacramento River WWTP data showed no relationships between effluent and influent inorganic mercury concentrations (with SRCSD: $R^2 = 0.0004$, $p>0.05$; without SRCSD: $R^2 = 0.0029$, $p>0.05$; Figure 50). No relationships were indicated by individual WWTP scatter plots as well, though some facilities were more effective at removing inorganic mercury (Figure 51 and Table 34). Scatter plots for SRCSD Sacramento River WWTP showed no significant relationships for the paired data collected from December 2000 to December 2004 (all data: $R^2 = 0.0004$, $p>0.05$; warm season: $R^2 = 0.0038$, $p>0.05$; cool season: $R^2 = 0.0045$, $p>0.05$; Figure 52); however, the scatter plots indicate that as influent concentrations increased, effluent concentrations did not increase.

The average effluent:influent inorganic mercury ratio for SRCSD Sacramento River WWTP was 5.1%; the ratio did not appear to change from December 2000 to December 2004 (Figure 53). The inorganic mercury removal efficiency during this period was consistently high with an average of about 95%, indicating that the SRCSD Sacramento River WWTP was effective in removing most of the inorganic mercury from the waste stream. As mentioned in Section 4.2.3, there was an observed decreasing trend in effluent inorganic mercury from WY2001-2007, particularly from 2005 to 2007. However, as indicated earlier, Board staff does not have influent inorganic mercury data after 2004 and was unable to compare effluent and influent concentrations during this later period.

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5 ESTIMATION OF METHYLMERCURY LOADS FROM CENTRAL VALLEY DISCHARGERS

In response to comments from the Sacramento Regional County Sanitation District on the May 2009 draft report, an additional chapter was added to this report to assess the relative contribution of methylmercury loading to the Delta from NPDES facilities in and upstream of the Delta. This chapter describes the methods used to calculate methylmercury and total mercury loads discharged by the different types of NPDES facilities and provides a brief review of loads by facility type and watershed.

All of the mass load calculations are based on the following equation:

$M_x = C_x * V$

Where: M_x = Mass of constituent, X

C_x = Concentration of constituent, X, in mass per volume

V = Volume of effluent

For example, the annual methylmercury load discharged for the Stockton WWTP was calculated as follows:

$M_x = (0.935 \text{ ng/l} \div 10^9) * (28 \text{ mgd} * 365 * 10^6 * 3.7854118) =$ **36 g/year**

Where: M_x = Mass of methylmercury (grams per year)

C_x = Concentration of methylmercury (ng/l) converted to grams per liter

V = Volume of effluent (million gallons per day) converted to liters per year

Not all facilities in the Central Valley were required to collect methylmercury and/or total mercury by the 2004 13267 Order or by their existing permit requirements. In addition, some facilities only recently began to discharge to surface water; some of these have collected effluent methylmercury and total mercury data and others have not. Table B.5 in Appendix B includes the effluent concentration and volume values used to estimate the loads discharged by each facility. For facilities that have not yet collected effluent total mercury or methylmercury concentration data, staff used the average of concentration data available for similar facilities to calculate the loads and noted where this was done in Table B.5.

Some facilities have ceased to discharge to surface water since effluent methylmercury and total mercury concentration data were collected. Data for such facilities, as well as data for facilities upstream of major dams, were included in the calculation of average methylmercury and total mercury concentrations by facility type used to estimate effluent loads for facilities with no effluent concentration data. Table B.5 does not

include all facilities located upstream of major dams because few of these were required to collect methylmercury data by the 2004 13267 Order. Also, Table B.5 includes several facilities for which total mercury data were available but methylmercury data were not, especially in the tributary watersheds upstream of major dams.

Tables 35 and 36 provide the sums of the annual total mercury loads and methylmercury loads, respectively, discharged by NPDES facilities within each discharger category in the Delta/Yolo Bypass and its tributary watersheds downstream of major dams. Table 37 compares the sum of annual methylmercury loads discharged by NPDES facilities to the sum of all point and nonpoint source methylmercury loading to each Delta subarea identified in the February 2010 Delta TMDL Staff Report (Wood *et al.*, 2010b, Table 8.4). As noted earlier, power, heating/cooling, and aquaculture facilities that use ambient water for cooling water do not appear to act as a net source of methylmercury to receiving waters and therefore are not included. GWF Power Systems is included because it acquires its intake water from sources other than ambient surface water. Only facilities that were discharging during the TMDL methylmercury load evaluation period (WY2000-2003) and/or the total mercury load evaluation period (WY1984-2003) were included in Tables 35, 36 and 37.

Effluent total mercury concentration data were not available for any of the facilities within the food, laboratories, and port terminal categories, and consequently these categories are not included in the load summaries described in Table 35. Because these facilities account for only about a quarter of a percent of the discharge volume from NPDES facilities in the Delta source region, they likely do not affect our understanding of relative contributions from different point and nonpoint sources.

As shown in Tables 35 and 36, about 96% (3,435 g/yr) of the total mercury loading from all NPDES facilities (3,586 g/yr) and more than 99% (228 g/yr) of the methylmercury loading from all NPDES facilities (229 g/yr) comes from municipal WWTPs. About 67% of the total mercury loading from all NPDES facilities and about 89% of the methylmercury loading from all NPDES facilities comes from facilities within the Delta/Yolo Bypass. A comparison of Table 36 to Table B.5 in Appendix B indicates that nearly 90% of the methylmercury loading from the 61 municipal WWTPs that discharge to the Delta and its tributary watersheds downstream of major dams comes from two WWTPs, the SRCSD Sacramento River WWTP (161 g/yr, 71%) and Stockton WWTP (36 g/yr, 16%). This is not surprising given the most populous urban areas in the Sacramento and San Joaquin Basins (the Delta's primary source region) – Sacramento in Sacramento County and Stockton in San Joaquin County – are adjacent to and within the Delta (CDOF, 2007; Wood *et al*., 2010b, Figure 6.9).

The Delta methylmercury TMDL divides the Delta into eight subareas based on the hydrologic characteristics and mixing of the source waters (Wood *et al.*, 2010b). A separate methylmercury reduction strategy was developed for each subarea because

the levels of impairment and the methylmercury sources in the subareas are substantially different (Wood *et al.*, 2010a and 2010b). Table 37 compares the methylmercury loads discharged by NPDES facilities within the Delta and its tributary watersheds downstream of major dams to the total methylmercury loading to each subarea from point and nonpoint sources within the Delta and its tributary inputs.

Overall, NPDES facilities account for about 4% of the methylmercury load to the Delta; NPDES facilities within the Delta contribute about 205 grams per year (g/year) while facilities in upstream watersheds that are downstream of major dams contribute about 24 g/year. The Delta TMDL divides the Delta into hydrologically-defined subwatershed areas; different sources supply the different areas. For example, NPDES facilities within the San Joaquin River and Sacramento River subareas contribute about 7-9% of all methylmercury loading to those subareas, while NPDES facilities within the Central Delta, West Delta, and Yolo Bypass subareas contribute less than 0.2% of all methylmercury loading to these subareas. For some receiving waters (e.g., in the Sacramento and San Joaquin subareas), reducing municipal WWTP methylmercury discharges, along with reductions from other point and nonpoint sources, may be an important component in reducing methylmercury levels in ambient water. For example, the Sacramento River is the largest river in California and drains a 27,000 square-mile area – almost one fifth of the State of California and about one half of the Central Valley – that contains numerous reservoirs and a myriad of point and nonpoint sources downstream of the reservoirs. As noted as early as 1997 in the Sacramento River Mercury Control Planning Project report prepared for SRCSD by Larry Walker Associates, "… mercury sources in the study area appear to be diffusely distributed without any significant "hotspots" …" (LWA, 1997, page 31). As a result, any individual discharge from a point or nonpoint source that provides a notable percentage (e.g., more than 1%) of methylmercury loading to the Sacramento River warrants evaluation.

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6 DISCUSSION & NEXT STEPS

The non-municipal NPDES facilities in the Delta source region typically had low effluent methylmercury concentrations (Table 17). Aquaculture and power generation facilities appeared to be neither significant sources nor sinks of methylmercury. More data is necessary to determine if the other facilities in these two categories and heating/cooling facilities are net methylmercury sources or sinks. The aggregate, paper/saw mills, groundwater remediation, drinking water treatment, and other non-municipal facilities were sources of methylmercury but typically had very low effluent methylmercury concentrations (average of 0.05 ng/L; see Table 17). Of the 198 effluent methylmercury samples submitted by non-municipal facilities, 134 were less than or equal to 0.05 ng/l, and 80 of those were below the method detection limit (typically less than 0.025 ng/l). The highest effluent methylmercury concentration observed in the non-municipal facilities was 1.91 ng/l from a stormwater detention pond at the SPI Shasta Lake Mill; all other sample results from the mill and other non-municipal facilities were less than 0.2 ng/l.

Municipal WWTPs contribute the most discharge (by volume and methylmercury load) to the Delta source region of any one facility category and had average effluent methylmercury concentrations that ranged from non-detect (<0.02 ng/l) to 2.9 ng/l, about a 150-fold difference. Twenty of the 61 Central Valley municipal WWTPs that submitted effluent data had average effluent concentrations less than 0.05 ng/l, and 13 WWTPs had averages less than 0.03 ng/l. In contrast, 18 WWTPs had average effluent methylmercury concentrations greater than 0.2 ng/l, and seven had averages greater than 1 ng/l.

To begin the process of evaluating whether and how methylmercury discharges from municipal WWTPs may be reduced, Board staff conducted a literature review. In addition, staff evaluated treatment process information for Central Valley municipal WWTPs and available methylmercury and inorganic mercury concentration data for influent and effluent. The reviews indicate several trends that merit additional investigation:

- Central Valley WWTPs that use treatment pond systems (oxidation, facilitative, settling or stabilization ponds) as a significant part of their treatment process had the highest effluent methylmercury concentrations. The “Pond + C/D” and “Pond + Filtration + C/D” treatment categories had significantly higher effluent methylmercury values than all other treatment categories, with one exception. The “Pond + Filtration + C/D” category did not have significantly higher effluent methylmercury concentrations than the “Secondary + C/D” category. Similarly in Canada, the West End WWTP, which was the only facility of the three City of Winnipeg treatment plants that has treatment ponds in its treatment process, also had higher effluent methylmercury concentrations than the other two City of Winnipeg treatment plants.

- Municipal WWTPs in the “Secondary + C/D” and “Pond + C/D” treatment categories had lower methylmercury removal efficiencies indicated by significantly higher effluent:influent ratios than WWTPs in all other treatment categories.
- Mercury-contaminated trickling filters at the Fritz Island WWTP in Pennsylvania acted as a substantial source of both inorganic mercury and methylmercury to the plant’s effluent. The average effluent methylmercury concentration at the Fritz Island WWTP was approximately 4 ng/l. Likewise in Central Valley WWTPs, within the “Secondary + C/D” and “Tertiary + C/D” treatment categories, the “Fixed Media” subcategory, which includes trickling filters, had average effluent methylmercury concentrations of 0.22 ng/l and 0.12 ng/l, respectively. Within the “Filtration + C/D” category, the “Fixed Media” subcategory had significantly higher effluent methylmercury concentrations than the “Activated Sludge” subcategory.
- Central Valley WWTPs that have some combination of nitrification/denitrification (N/D), filtration, and ultraviolet (UV) disinfection generally had lower effluent methylmercury concentrations. The “N/D + Filtration + C/D”, “Secondary w/ N/D + UV”, “N/D + Filtration + UV”, “Filtration + UV”, “Secondary w N/D + C/D” and “Filtration + C/D” treatment categories all had significantly lower effluent methylmercury concentrations than the “Secondary + C/D”, “Pond + C/D” and “Pond + Filtration +C/D” categories. In addition, the “N/D + Filtration + C/D” category had significantly lower effluent methylmercury concentrations than the “Secondary w/ N/D + C/D” and “Filtration + C/D” categories, suggesting that both the filtration and nitrification/denitrification treatment processes may have played a role in the decrease in the methylmercury concentrations of these facilities.
- Each secondary treatment subcategory within the “Filtration + C/D” category had significantly lower average and median effluent methylmercury concentrations than the same subcategory within the “Secondary + C/D” category, which suggests that the filtration treatment process may have assisted in the reduction of methylmercury in the effluent of these facilities.
- Several published studies investigated methylmercury at WWTPs that use conventional activated sludge treatment. The effluent methylmercury concentrations were variable with averages of 0.04 ng/l at the San Jose/Santa Clara WWTP, 0.2 ng/l to greater than 2 ng/l at the West End WWTP in Canada, and 1.53 ng/l at the Onondaga County Metropolitan WWTP in New York. Treatment ponds are used at the West End WWTP in Winnipeg, which could explain the elevated effluent methylmercury. The Onondaga County WWTP had an average influent methylmercury concentration of 5.05 ng/l and a removal efficiency of 70%. The methylmercury removal efficiency of the SJ/SC WWTP was 97%. The higher methylmercury removal efficiency of the SJ/SC WWTP could have been due to differences in other treatment processes. Nitrification and denitrification are incorporated in the activated sludge process of the SJ/SC WWTP and tertiary filtration is used as well, while neither is used in the Onondaga County WWTP.
- The SRCSD Sacramento River WWTP and SJ/SC WWTP had similar average influent methylmercury concentrations (1.55 ng/l and 1.6 ng/l, respectively).

However, the SJ/SC WWTP secondary treatment resulted in a much lower average secondary effluent methylmercury concentration (0.05 ng/l) than the SRCSD WWTP (0.38 ng/l). The secondary treatment process of the SRCSD Sacramento River facility is pure oxygen activated sludge without nitrification and denitrification. The differences in methylmercury removal efficiency between the two WWTPs may be either due to the pure oxygen activated sludge, nitrification/denitrification or both.

- The San Jose/Santa Clara WWTP study observed a methylmercury removal efficiency of 40% between the tertiary filter influent (0.05 ng/l) and final effluent (0.03 ng/l). Given the low concentrations, this is a small reduction when compared to the methylmercury removal efficiency of 96% between the secondary influent (1.3 ng/l) and secondary effluent (0.05 ng/l) (see Table 2). This suggests that most of the methylmercury removal occurred during the secondary treatment process.
- Significant relationships between influent and effluent methylmercury concentrations existed for all the paired data from the Central Valley WWTPs. This indicates that reductions in methylmercury in the effluent were in part due to lower influent concentrations. However, 7-13% of the variability in effluent methylmercury concentrations was explained by influent concentrations, indicating that effluent concentrations were affected by other factors as well.
- Seasonal variability was observed in effluent methylmercury concentrations at several Central Valley WWTPs, as well as WWTPs evaluated elsewhere. The City of Winnipeg's West End Plant, which utilizes conventional activated sludge and treatment ponds, had a seasonal trend in its effluent methylmercury concentrations, while its two other plants, which use pure oxygen activated sludge and no treatment ponds, did not have a seasonal trend. At the West End Plant, methylmercury concentrations increased as ambient temperatures increased, with the highest concentration occurring in August. The Onondaga County Metropolitan WWTP, which uses conventional activated sludge, demonstrated that warm temperatures were a catalyst for the methylation process to occur, apparently in both the environment as well as through the treatment process. For the several Central Valley WWTPs where seasonal variability was observed, the effluent methylmercury concentrations were higher in the warm season (e.g., May through November), and lower in the cool season. No obvious relationship between seasonality and the treatment processes of the Central Valley WWTPs seemed to exist.
- Methylmercury production occurred during the secondary activated sludge treatment process at the Onondaga County WWTP. McAlear (1996) hypothesized that mercury methylation occurred in anoxic micro-zones within the activated sludge flocs. A correlation between high concentrations of biological solids and mercury methylation during the activated sludge process was discovered at the Whitlingham Sewage Treatment Works (Goldstone *et al.*, 1990).
- The SRCSD study demonstrated that the removal of solids may have been a removal mechanism for methylmercury; however, inorganic mercury had a greater particle affinity than methylmercury and was removed more efficiently by solids

removal (Parmer *et al.*, 2005). In the Whitlingham Sewage Treatment Works study, the centrifugation and filtration of return activated sludge samples indicated that methylmercury had a greater affinity for the particulate phase of the return activated sludge than for the soluble phase. From the literature reviewed, it appears that the inorganic mercury and methylmercury removed from wastewater is partially due to the removal of solids, with the mechanism being more efficient for inorganic mercury. Board staff did not evaluate this relationship further for the Central Valley WWTPs because of their limited data set; however, this merits additional investigation.

- SRCSD WWTP's influent methylmercury concentrations and effluent inorganic mercury and methylmercury concentrations and loads decreased between 2001 and 2007. This decrease was attributed to a decrease in influent inorganic mercury associated with the initiation of SRCSD's "Be Mercury Free" source control program. No similar pattern was noted between influent inorganic mercury and effluent methylmercury at any other WWTP in the Central Valley.

Municipal WWTPs have multiple treatment processes and the factors affecting methylmercury production and degradation are complex. As a result, the differences in effluent methylmercury concentrations among the Central Valley WWTPs are most likely due to multiple factors and different combinations of treatment processes. Furthermore, a few of the treatment categories evaluated contained only one or two WWTPs, resulting in a limited data set for those categories. Therefore, the data of some of the treatment categories may not be representative of other WWTPs that utilize the same treatment processes. Also, of the 61 WWTPs that submitted effluent methylmercury data, only 23 submitted influent methylmercury data, and only nine submitted influent inorganic mercury data. Therefore, comparisons among WWTPs and treatment categories were done without correcting for influent inorganic mercury and methylmercury concentrations. In addition, influent inorganic mercury and methylmercury concentrations often had substantial day-to-day variability. As a result, comparisons between influent and effluent samples collected on the same day may not be appropriate, depending on the residence time of the wastewater in a particular plant.

The Central Valley Clean Water Association (CVCWA) has conducted a preliminary evaluation of effluent methylmercury data for a subset of WWTPs evaluated in this report. CVCWA's preliminary evaluation similarly found that WWTPs that incorporate any significant effluent storage (e.g., ponds) have higher methylmercury concentrations, and WWTPs with activated sludge treatment processes that result in a fully-denitrified, low ammonia effluent also have lower effluent methylmercury concentrations (Pirondini, 2008b). After completing the QA/QC review of the available effluent and influent methylmercury concentration data (see Chapter 3), Board staff forwarded the completed database to CVCWA so that they could continue a more detailed evaluation.

Additional analyses are needed to continue the evaluation of potential relationships between WWTP treatment processes, mercury minimization measures for mercury

sources to WWTP influent, and effluent methylmercury levels. Board staff and WWTP staff and consultants have informally discussed several ideas for future analyses and key questions to be addressed by those analyses. Some analyses would not require additional influent and effluent sampling, for example:

- Conduct more detailed, focused analyses of the data presented in this report.
- Gather more information about the influent and effluent samples described in this report, for example (but not limited to): specific sampling locations, depths, and time of day; influent inorganic mercury concentrations; pH, alkalinity, dissolved oxygen, temperature, and nitrate, sulfate and ammonia concentrations; and specific treatment processes in place at the time of sample collection.
- Do other factors impact reported concentrations, such as sampling protocols including location, time of day, holding time and composite vs. grab samples?

In addition, the data set presented in this report needs to be updated, with special attention given to facilities that have recently completed treatment process upgrades. For example, the City of Stockton WWTP was upgraded to meet new ammonia effluent limits and Title 22 (or equivalent) tertiary requirements since the data presented in this report were collected. The average effluent methylmercury and total mercury concentrations for January-July 2009 are about 91% and 83% lower than the annual average methylmercury and total mercury concentrations, respectively, observed in 2004/2005. It is not known if the treatment plant upgrades are responsible for the total mercury and methylmercury reductions, or if the reductions are a result of other operational or physical changes. Additional sampling may be needed to determine the cause of the decrease. In addition, methylmercury results for only seven monthly effluent samples have been submitted since the upgrades were completed. As more data are collected, Board staff will work with City of Stockton staff to evaluate whether the above trends are representative of current conditions.

Also, at the time this report was receiving final review, reports for Phases 1 and 2 of the WERF-funded project, "Estimation of Mercury Bioaccumulation Potential from Wastewater Treatment Plants in Receiving Waters", were released (Dean and Mason, 2009a and 2009b). This project assessed changes in mercury bioavailability in wastewater effluents and receiving waters and developed a guidance document for wastewater treatment professionals who want to assess the bioavailability of mercury in their wastewater, compare it to other point and nonpoint sources, and assess changes in bioavailability in their effluent when it is mixed in a receiving water body. The Phase 1 and 2 reports should be considered by future wastewater analyses and control studies, as well as when the Delta mercury TMDL control program goes through future reviews during its implementation.

After additional analyses of existing data are completed, it may be useful to conduct targeted monitoring and pilot scale studies where actual sewage flow may be used to evaluate specific treatment processes and variations.

Possible questions that could be addressed by future analyses include, but are not limited to, the following:

- Do relationships exist between nitrate, ammonia, sulfate, sulfite and TSS concentrations and methylmercury concentrations throughout the treatment process? If so, could treatment processes designed to reduce effluent ammonia also reduce effluent methylmercury?
- Are tertiary treatment processes effective in significantly reducing methylmercury concentrations within a WWTP? What are the affects of filtration and UV treatment on effluent methylmercury?
- Why do some WWTPs have seasonality in their effluent methylmercury concentrations and others do not? What are the causes behind the seasonality observed in methylmercury concentrations?
- Do influent and effluent methylmercury concentrations have any diurnal variability, and if so, what are the causes?
- Is it feasible to modify the biological secondary processes at some plants to increase methylmercury degradation? If so, can "real-time" indicators (e.g., pH or alkalinity) be developed so that plant operators can make immediate adjustments (versus having to wait several weeks for methylmercury analyses)?
- Do WWTPs that use pond systems or other treatments act as greater sources of inorganic mercury and/or methylmercury than WWTPs that utilize other treatment systems?
- How much are effluent inorganic mercury and methylmercury concentrations reduced by reducing influent inorganic mercury concentrations and/or loads (e.g., by implementing inorganic mercury source minimization measures)?

Several Central Valley WWTP staff and consultants have noted that it would be very helpful to establish a working group that coordinates efforts between CVCWA, San Francisco Bay area facilities, and other regional efforts to develop more detailed analyses of the existing information, further evaluate treatment processes, and design additional monitoring studies and pilot projects. Board staff is supportive of this concept and will work with dischargers and working groups to design and review studies.

7 REFERENCES

Balogh, S. and L. Liang. 1995. Mercury Pathways in Municipal Wastewater Treatment Plants. *Water, Air, and Soil Pollution,* 80: 1181-1190.

Bodaly, R.A., J.W.M. Rudd, and R.J. Flett. 1998. Effect of Urban Sewage Treatment on Total and Methyl Mercury Concentrations in Effluents. *Biogeochemistry*, 40: 279-291.

Bosworth, D.H. 2008. *Six-year Comparison of Methylmercury Loads of SRCSD Sacramento River WWTP and its Receiving Water*. Memorandum from David H. Bosworth (Environmental Scientist, CVRWQCB) to Patrick W. Morris (Senior WRC Engineer, Mercury TMDL Unit, CVRWQCB), November 20, 2008.

Byington, A., K. Coale, G. Gill, and K. Choe. 2005. *Photo-degradation of Methyl Mercury (MMHg) in the Sacramento – San Joaquin Delta: A Major Sink.* Poster Presentation, Celebrating Science Stewardship, State of the San Francisco Estuary Conference, 7th Biennial, October 4-6, 2005, Oakland, CA.

CDFG. 2002. Quality Assurance Management Plan for the State of California's Surface Water Ambient Monitoring Program: "SWAMP". Prepared by M. Puckett California Department of Fish and Game, Monterey, CA, prepared for the California State Water Resources Control Board. December 2002. Available at: http://www.waterboards.ca.gov/swamp/qamp.html.

CDOF. 2007. New State Projections Show 25 Million More Californians by 2050; Hispanics to Be State's Majority Ethnic Group by 2042. California Department of Finance (CDOF), Sacramento, California, July 2007. Table 1: County Total Population by Decade. (Updated since May 2004 publication.) Available at: http://www.dof.ca.gov/HTML/DEMOGRAP/ReportsPapers/Projections/P1/P1.asp. Accessed: July 13, 2007.

CMP. 2004. Microsoft Access database of Coordinated Monitoring Program water quality data through August 2003. Database and updates provided by Larry Walker Associates (Mike Trouchon) and Sacramento Regional County Sanitation District (Steve Nebozuk, CMP Program Manager) to Central Valley Regional Water Quality Control Board (Michelle Wood, Environmental Scientist, Sacramento).

Dansereau, M., N. Lariviere, D. Du Tremblay, and D. Belanger. 1999. Reproductive performance of two generations of female semidomesticated mink fed diets containing organic mercury contaminated freshwater fish. *Archives of Environmental Contamination and Toxicology*, 36: 221-226.

Davis, J.A., B.K. Greenfield, G. Ichikawa, and M. Stephenson. 2008. Mercury in sport fish from the Sacramento San Joaquin Delta region, California, USA. *Science of the Total Environment*, 391:66-75.

Davis, J.A, B.K. Greenfield, G. Ichikawa and M. Stephenson. 2003. *Mercury in Sport Fish from the Delta Region.* Final report submitted to the CALFED Bay-Delta

Program for the project: An Assessment of the Ecological and Human Health Impacts of Mercury in the Bay-Delta Watershed (Task 2A). San Francisco Estuary Institute and Moss Landing Marine Laboratories. Available at: http://loer.tamug.tamu.edu/calfed/FinalReports.htm.

Davis, J.A., M.D. May, G. Ichikawa, and D. Crane. 2000. *Contaminant Concentrations in Fish from the Sacramento-San Joaquin Delta and Lower San Joaquin River – 1998.* San Francisco Estuary Institute report. Richmond, California. September 2000.

Dean, J.D. and R.P. Mason. 2009a. Estimation of Mercury Bioaccumulation Potential from Wastewater Treatment Plants in Receiving Waters: Phase I. Research developed by J. David Dean (ArcTellus) and Robert P. Mason (University of Connecticut), funded and copyrighted by the Water Environment Research Foundation (WERF) [Alexandria, VA, USA], co-published by IWA Publishing [London], and developed in part by the U.S. Environmental Protection Agency through Cooperative Agreement No. CR83155901-1.

Dean, J.D. and R.P. Mason. 2009a. Estimation of Mercury Bioaccumulation Potential from Wastewater Treatment Plants in Receiving Waters: Phase II. Research developed by J. David Dean (ArcTellus) and Robert P. Mason (University of Connecticut), funded and copyrighted by the Water Environment Research Foundation (WERF) [Alexandria, VA, USA], co-published by IWA Publishing [London], and developed in part by the U.S. Environmental Protection Agency through Cooperative Agreement No. CR83155901-1.

Foe, C., S. Louie, and D. Bosworth. 2007. Methylmercury Concentrations and Loads in the Sacramento River Basin and San Joaquin River Basin. Posters presented at the 8th Biennial State of the San Francisco Estuary Conference, October 16-17, 2007, Oakland, CA.

Foe, C., S. Louie, and D. Bosworth. 2008. *Methylmercury Concentrations and Loads in the Central Valley and Freshwater Delta.* Final Report submitted to the CALFED Bay-Delta Program for the project “Transport, Cycling and Fate of Mercury and Monomethylmercury in the San Francisco Delta and Tributaries” Task 2. Central Valley Regional Water Quality Control Board. Available at: http://mercury.mlml.calstate.edu/reports/reports/

Gill, G. 2008. *Monomethylmercury Photodegradation Studies*. Final Report submitted to the CALFED Bay-Delta Program for the project “Transport, Cycling and Fate of Mercury and Monomethylmercury in the San Francisco Delta and Tributaries” Task 5.1. California Department of Fish and Game Moss Landing Marine Laboratories and Pacific Northwest National Laboratory. Available at: http://mercury.mlml.calstate.edu/reports/reports/

Gilmour, C.C. and N.S. Bloom. 1995. A Case Study of Mercury and Methylmercury Dynamics in a Hg-Contaminated Municipal Wastewater Treatment Plant. *Water, Air, Soil Pollution*, 80: 799-803.

Goldstone, M.E., C. Atkinson, P.W.W. Kirk and J.N. Lester. 1990. The behavior of heavy metals during wastewater treatment, III. Mercury and Arsenic. *The Science of the Total Environment*, 95: 271-294.

Huber, K. 1997. *Wisconsin Mercury Sourcebook: A Guide to Help Your Community Identify & Reduce Releases of Elemental Mercury*. Wisconsin Department of Natural Resources, Bureau of Watershed Management. Madison, WI. May 1997. Available at: http://www.epa.gov/glnpo/bnsdocs/hgsbook/.

LWA. 1997. *Sacramento River Mercury Control Planning Project.* Final project report prepared for the Sacramento Regional County Sanitation District by Larry Walker Associates (LWA). March.

LWA. 2002. Strategic Plan for the Reduction of Mercury-Related Risk in the Sacramento River Watershed. Appendix 1: Mercury Conceptual Model Report – Mercury Quantities, Fate, Transport, and Uptake in the Sacramento River Watershed. Prepared by Larry Walker Associates (LWA), Davis, California, for Delta Tributaries Mercury Council and Sacramento River Watershed Program. December 2002.

Marvin-DiPasquale, M.M., J. Agee, R.S. Oremland, M. Thomas, D.P. Krabbenhoft and C.G. Gilmour. 2000. Methylmercury Degradation Pathways - A comparison among three mercury impacted ecosystems. *Environmental Science & Technology*, 34: 4908-4916.

McAlear, J.A. 1996. *Concentrations and Fluxes of Inorganic mercury and Methylmercury Within a Wastewater Treatment Plant*. Syracuse, NY: Syracuse University, Masters thesis.

Metcalf and Eddy, Inc. 1972. *Wastewater Engineering: Collection, Treatment, Disposal.* New York, NY: McGraw-Hill Book Company, 662-665 p.

NRC. 2000. *Toxicological Effects of Methylmercury*. National Research Council, Committee on the Toxicological Effects of Methylmercury (NRC). Washington, D.C.: National Academy Press. Available at: http://www.nap.edu/books/0309071402/html.

Parmer A., M. Maidrand, V. Fry, K. Abu-Saba, and L. Whalin. 2005. *Methylmercury Fate and Transport Study*. Sacramento Regional County Sanitation District, Elk Grove, CA; and Larry Walker Associates, Davis, CA.

Pavlogeorgatos, G.D., N.S. Thomaidis, A.D. Nikolaou, and T.D. Lakkas. 2006. Determination of Methyl Mercury in a Pilot-Scale Activated Sludge Wastewater Treatment Plant. *Global NEST Journal*, 8 (1): 61-67.

Pirondini, T. 2008a. Electronic mail from Tony Pirondini (Laboratory Supervisor, Vacaville Water Quality Laboratory) to Michelle Wood (Environmental Scientist, California Regional Water Quality Control Board, Central Valley Region, Sacramento), on March 12, 2008, regarding the effects of nitrification and denitrification on methylmercury in WWTPs.

Pirondini, T. 2008b. “Comparison of Methylmercury (MeHg) in Effluents vs. Wastewater Treatment Processes”. Preliminary evaluation by the Central Valley Clean Water Agencies dated 20 February 2007. Provided in a Microsoft Excel file by Tony Pirondini (Laboratory Supervisor, Vacaville Water Quality Laboratory) to Michelle Wood (Environmental Scientist, California Regional Water Quality Control Board, Central Valley Region, Sacramento).

Puckett, H.M. and B.H. van Buuren. 2000. *Quality Assurance Project Plan for the CALFED Mercury Project*. California Department of Fish and Game, Granite Canyon Marine Pollution Studies Laboratories, Monterey, CA; and Frontier Geosciences, Inc., Seattle, WA. March 2000.

Regnell, O., A. Tunlid, G. Ewald and O. Sangfors. 1996. Methyl mercury production in freshwater microcosms affected by dissolved oxygen levels: role of cobalamin and microbial community composition. *Canadian Journal of Fish and Aquatic Sciences*, 53: 1535-1545

Regnell, O., T. Hammar, A. Helgée and B. Trodesson. 2001. Effects of anoxia and sulfide on concentrations of total and methylmercury in sediment and water in two Hg-polluted lakes. *Canadian Journal of Fish and Aquatic Sciences*, 58: 506-517.

Sellers, C., and C.A. Kelly. 2001. Fluxes of methylmercury to the water column of a drainage lake: The relative importance of internal and external sources. *Limnology and Oceanography*, 46: 623-631.

Sellers, C., C.A. Kelly, and J.W.M. Rudd. 1996. Photodegradation of methylmercury in lakes. *Nature*, 380: 694-697.

SFEI. 2007. The San Francisco Bay Mercury News. Volume 4, Number 1. Winter 2007. Available at: http://www.sfei.org/rmp/mercury_newsletter/HgNewsletterWinter2007.pdf.

SJ/SC. 2007. *San Jose/Santa Clara Water Pollution Control Plant Mercury Fate and Transport Study.* Environmental Services Department, SJ/SC Water Pollution Control Plant. San Jose, CA. March 2007.

Slotton, D.G., S.M. Ayers, T.H. Suchanek, R.D. Weyland, A.M. Liston, C. Asher, D.C. Nelson, and B. Johnson. 2003. *The Effects of Wetland Restoration on the Production and Bioaccumulation of Methylmercury in the Sacramento-San Joaquin Delta, California.* Final report submitted to the CALFED Bay-Delta Program for the project: An Assessment of the Ecological and Human Health Impacts of Mercury in the Bay-Delta Watershed. University of California, Davis, Dept. of Environmental Science and Policy, Dept. of Wildlife, Fish and Conservation Biology, and Division of Microbiology; U.S. Fish and Wildlife Service, Division of Environmental Contaminants.

Slotton, D.G., S.M. Ayers, and R.D. Weyland. 2007. *CBDA Biosentinel Mercury Monitoring Program, Second Year Draft Data Report Covering Sampling Conducted February through December 2006*. May 29, 2007. Available at: http://www.sfei.org/cmr/fishmercury/DocumentsPage.htm

SRCSD. 2004. *Sacramento Regional Sanitation District Source Control Summary Report*. Sacramento Regional Sanitation District. December 2004.

SRCSD. 2005. *Sacramento Regional Sanitation District Source Pollutant Accounting Mass Balance for Metals and Total Dissolved Solids*. Sacramento Regional Sanitation District. May 2005.

SRCSD. 2008. Localized Mercury Bioaccumulation Study. Final report prepared for Sacramento Regional County Sanitation District (SRCSD) by Larry Walker

Associates in association with Applied Marine Sciences, Studio Geochimica, and University of California, Davis. March 2008.

Stephenson, M., C. Foe, G.A. Gill, and K.H. Coale. 2008. Transport, Cycling, and Fate of Mercury and Monomethyl Mercury in the San Francisco Delta and Tributaries: An Integrated Mass Balance Assessment Approach. CALFED Mercury Project Final Report. Available at: http://mercury.mlml.calstate.edu/reports/reports/

Tetra Tech, Inc. 2005. *Guadalupe River Watershed Mercury TMDL Project Final Conceptual Model Report.* Prepared by Tetra Tech, Inc., Research and Development, Lafayette, CA. Prepared for San Francisco Bay Regional Water Quality Control Board. 20 May 2005. 160 p.

USEPA. 2002. Guidance for Quality Assurance Project Plans EPA QA/G-5. U.S. Environmental Protection Agency (USEPA), Office of Environmental Information (USEPA). EPA-240-R-02-009. December 2002.

Wiener, J.G., C.C. Gilmour and D.P. Krabbenhoft. 2003a. *Mercury Strategy for the Bay-Delta Ecosystem: A Unifying Framework for Science, Adaptive Management, and Ecological Restoration.* Final Report to the California Bay Delta Authority for Contract 4600001642 between the Association of Bay Area Governments and the University of Wisconsin-La Crosse, 31 December 2003.

Wiener, J.G., Krabbenhoft, D.P. Heinz, G.H., and Scheuhammer, A.M. 2003b. Ecotoxicology of Mercury, Chapter 16. *In* Handbook of Ecotoxicology, 2nd Edition. D.J. Hoffman, B.A. Rattner, G.A. Burton, Jr., and J. Cairns, Jr. (editors). Boca Raton, Florida: CRC Press, pp. 409-463.

Wiener, J.G. and D.J. Spry. 1996. Toxicological Significance of Mercury in Freshwater Fish (Chapter 13). *In*: Environmental Contaminants in Wildlife: Interpreting Tissue Concentrations. SETAC Special Publication. W.N. Beyer, G.H. Heinz and A.W. Redmon-Norwood. Boca Raton: CRC Press, Inc, pp. 297-339.

Wolfe, M.F., S. Schwarzbach and R.A. Sulaiman. 1998. Effects of mercury on wildlife: A comprehensive review. *Environmental Toxicology and Chemistry*, 17:146-60.

Wood, M., P. Morris, J. Cooke, and S. Louie. 2010a. Amendments to The Water Quality Control Plan for the Sacramento River and San Joaquin River Basins for the Control of Methylmercury and Inorganic mercury in the Sacramento-San Joaquin Delta Estuary. Central Valley Regional Water Quality Control Board, Draft Staff Report for Public Review. Sacramento. February. Available at: http://www.waterboards.ca.gov/centralvalley/water_issues/tmdl/central_valley_projects/delta_hg/april_2010_hg_tmdl_hearing/index.shtml

Wood, M., C. Foe, J. Cooke, and S. Louie. 2010b. Sacramento – San Joaquin Delta Estuary TMDL for Methylmercury, Draft Staff Report for Public Review. Sacramento. February. Available at: http://www.waterboards.ca.gov/centralvalley/water_issues/tmdl/central_valley_projects/delta_hg/april_2010_hg_tmdl_hearing/index.shtml

TABLES

Table 1: Summary of Literature Review

Facility	Citation	Secondary Treatment	Tertiary Treatment (if any)	Influent MeHg (ng/l)	Influent MeHg: TotHg Ratio [(a)]	Post-Secondary Treatment MeHg (ng/l)	Post-Secondary Treatment MeHg:TotHg Ratio [(a)]	Final Effluent MeHg (ng/l)	Final Effluent MeHg: TotHg Ratio [(a)]	Comments
San Jose / Santa Clara Water Pollution Control Plant	SJ/SC, 2007	Activated sludge with nitrification/ denitrification	Filtration	1.57	0.94%	0.05	0.87%	0.04	2.0%	
Sacramento Regional Wastewater Treatment Plant	Parmer and others, 2005	Pure oxygen activated sludge		1.55	0.80%	0.38	7.7%	0.55	12%	180 MGD activated sludge plant. Slight rise in final effluent MeHg.
City of Winnipeg: North End, West End & South End Water Pollution Control Centres	Bodaly and others, 1998	North and South End: Pure oxygen activated sludge West End: Conventional diffused air activated sludge	West End only: Treatment lagoons	Average of all three plants: 2.2 (range: 0.5 - >4)		Not reported		North and South End: 0.13 - 0.56 West End: 0.2 - >2		Pure oxygen aeration exhibited greater removal efficiency of MeHg in effluent.
Pilot-scale activated sludge plant	Pavlogeor-gatos and others, 2006	Activated sludge		<70 (MDL: 0.07 µg/l)				<70 (MDL: 0.07 µg/l)		Pilot scale activated sludge study using synthetic wastewater containing glucose and ammonia. Spiked Hg concentrations of 10, 100, and 500 µg/l added directly to aeration tanks. No RAS; secondary sludge returned to aeration tanks.
Onondaga County Metropolitan Wastewater Treatment Plant	McAlear, 1996	Activated sludge	Phosphorous removal (addition of $FeSO_4$)	5.05	1.84%	2.76	21%	1.53	8.3%	
Fritz Island Wastewater Treatment Plant	Gilmore and Bloom, 1995	Trickling filters		3.0	1.92%	9.1	3.2%	4.0	3.7%	

Table 1: Summary of Literature Review

Facility	Citation	Secondary Treatment	Tertiary Treatment (if any)	Influent MeHg (ng/l)	Influent MeHg: TotHg Ratio [(a)]	Post-Secondary Treatment MeHg (ng/l)	Post-Secondary Treatment MeHg:TotHg Ratio [(a)]	Final Effluent MeHg (ng/l)	Final Effluent MeHg: TotHg Ratio [(a)]	Comments
Whitlingham Sewage Treatment Works	Goldstone and others, 1990	Activated sludge		11		120		< 10		

[(a)] Staff calculated the MeHg:TotHg ratios for the SJ/SC WWTP and Fritz Island WWTP studies using the average inorganic mercury and methylmercury data provided in their respective reports. The ratios for the SRCSD WWTP and Onondaga County WWTP studies were obtained from the reports.

Table 2: Total Mercury and Methylmercury Concentrations at the San Jose/Santa Clara WWTP

Sample Location	Average TotHg Conc. (ng/l)	Average Dissolved TotHg Conc. (ng/l)	Average MeHg Conc. (ng/l)	MeHg:TotHg Ratio [c]
Raw Sewage	168	2.9	1.6	0.9%
Primary Effluent	92	4.0	1.5	1.6%
Secondary Influent [a]	79	3.6	1.3	1.6%
Secondary Effluent [b]	5.2	1.1	0.05	0.87%
Filter Influent	5.1	1.2	0.05	0.98%
Tertiary Filter Effluent	1.6	1.2	0.03	1.9%
Filter Backwash	1.9	2.1	0.11	5.8%
Final Effluent	2.0	1.4	0.04	2.0%

[a] The SJ/SC WWTP study refers to the secondary influent as "Settled Sewage Influent to Secondary Units".
[b] The secondary treatment process consists of two pathways that are identical in function (biological nutrient removal) and receive the same influent. These numbers are averages of the effluent concentrations of the two pathways.
[c] Staff calculated the MeHg:TotHg ratio from the inorganic mercury and methylmercury data provided in the report.

Table 3: Phase 1A and 1B Total Mercury Concentrations, Mass Loads and Particulate Concentrations at the SRCSD Sacramento WWTP

Location [a]	Average TotHg Conc. (ng/l)	TotHg Mass Load (g/day)	TotHg Particulate Concentration (ng/g) [b]
Influent	192.33	131	1100
Primary Effluent	50.91	35	490
Mixed Liquor	693.33	660	408
Secondary Effluent	4.92	3.3	300
Dechlorinated Final Effluent	4.64	3	305
Waste Activated Sludge	1800	35.13	
Digested Sludge	12,333	60.36	800
Green SSB	170		350
Black SSB	430		770
Harvest SSB	990		1700
BRF Influent	13,166.67	23.92	800
SSB Return Flow	253.33	4.24	740
BRF Return Flow	150.67	0.47	580

[a] SSB: Solids Storage Basins BRF: Biosolids Recycling Facility
[b] Inorganic mercury particulate concentrations obtained from Table 9 in the SRCSD report.

Table 4: Phase 1A and 1B Methylmercury Concentrations, Mass Loads and Particulate Concentrations at SRCSD

Location [a]	Average MeHg Conc. (ng/l)	MeHg Mass Load (g/day)	MeHg Particulate Conc. (ng/g) [b]	MeHg:TotHg Ratio
Influent	1.55	1.06	4.93	0.80%
Primary Effluent	1.34	0.91	7.3	2.6%
Mixed Liquor	11.77	11.2	6.5	
Secondary Effluent	0.38	0.26	20.4	7.7%
Dechlorinated Final Effluent	0.55	0.36	33	12%
Waste Activated Sludge	30.72	0.5988	6.2	
Digested Sludge	245.88	1.176	13.01	
Green SSB	4.66		9.5	
Black SSB	18.35		32.4	
Harvest SSB	13.05		22	
BRF Influent	208.2	0.3585	13.5	
SSB Return Flow	7.39	0.1207	19	2.9%
BRF Return Flow	7.21	0.0215	24.2	5.5%

[a] SSB: Solids Storage Basins BRF: Biosolids Recycling Facility
[b] Methylmercury particulate concentrations obtained from Table 9 in the SRCSD report.

Table 5: Average Total Mercury, Methylmercury and TSS concentrations at the Onondaga County WWTP for the Entire Sampling Period (October 1995 to September 1996)

Location	Average TotHg Conc. (ng/l)	Average MeHg Conc. (ng/l)	MeHg:TotHg Ratio	Average TSS Conc. (mg/l)
Plant Influent	308	5.05	1.8%	206
Primary Effluent	112	1.92	2.2%	88.5
Secondary Effluent	24.0	2.76	21%	26.2
“Tertiary” Effluent	32.9	2.63	14%	9.48
Final Effluent	36.8	1.53	8.3%	11.7

Table 6: Seasonal Average Methylmercury Concentrations at the Onondaga County WWTP [(a)]

Location	Average Cold Weather (November to April) MeHg Conc. (ng/l)	Average Warm Weather (May to October) MeHg Conc. (ng/l)
Plant Influent	2.34	7.76
Primary Effluent	2.03	1.77
Secondary Effluent	1.94	3.49
"Tertiary" Effluent	2.40	2.87
Final Effluent	1.43	1.63

[(a)] Staff calculated the primary, secondary and "tertiary" effluent average concentrations for both the warm and cold weather periods from raw data provided in the Appendix of the report.

Table 7: Total Mercury and Methylmercury Concentrations in the Fritz Island WWTP Inputs and Outputs

Location	Total Mercury			Methylmercury		
	# of Samples [(a)]	Conc. Range (ng/l)	Average Conc. (ng/l)	# of Samples [(a)]	Conc. Range (ng/l)	Average Conc. (ng/l)
Plant Influent	3	185 - 556	358	3	1.36 - 2.45	1.91
Plant Effluent	3	108 - 448	228	3	4.03 - 5.69	4.74
Plant Sludge	3	3.96 - 4.09 [(b)]	4.02 [(b)]	3	1.6 - 5.2 [(b)]	3.23 [(b)]

[(a)] Each sample was a triplicate sample.
[(b)] The unit of measure for the wet weight sediment concentrations is μg/g.

Table 8: Total Mercury and Methylmercury Loads in the Inputs and Outputs of the Fritz Island WWTP

Site	TotHg Load (g/day)	Percent of TotHg Output Load from WWTP [(a)]	MeHg Load (g/day)	Percent of MeHg Output Load from WWTP [(a)]
Plant Influent	19.3		0.104	
Effluent	12.8	8%	0.269	68%
Sludge	144	92%	0.125	32%
Output Load from WWTP (Effluent + Sludge)	157	100%	0.394	100%
Net Output Load generated inside the WWTP (Output - Influent)	138	88%	0.29	74%

[(a)] The output load from the WWTP is equal to the sum of the effluent and sludge loads.

Table 9: Total Mercury and Methylmercury Concentrations in the Influent and Effluent of Various Components of the Fritz Island WWTP Treatment Processes

Site	TotHg Conc. (ng/l)	MeHg Conc. (ng/l)	MeHg:TotHg Ratio [(a)]
Plant Influent	**156**	**3**	**1.9%**
1st Stage Trickling Filters			
Input	229	7.8	3.4%
Output TF# 1	5660	31.9	0.56%
Output TF# 3	1540	24	1.6%
Intermediate Settling			
Input	2670	29.4	1.1%
Output	215	13	6.1%
Sludge	114,000 mg/kg	71 mg/kg	0.06%
2nd Stage Trickling Filters			
Input	215	13	6.1%
Output TF# 4	629	33.9	5.4%
Output TF# 5	291	10.8	3.7%
Output TF# 6	394	13.1	3.3%
Post 2nd Stage Settling			
Input	288	9.1	3.2%
Output	167	11.1	6.7%
Sludge	39,600 mg/kg	287 mg/kg	0.72%
Aeration			
Input	167	11.1	6.7%
Output	148	4.7	3.2%
Final Settling			
Input	148	4.7	3.2%
Output	76	6.9	9.1%
Sludge	124,000 mg/kg	205 mg/kg	0.17%
Final Effluent	**108**	**4**	**3.7%**

[(a)] Staff calculated the MeHg:TotHg ratio from the inorganic mercury and methylmercury data provided in the report.

Table 10: Summary of Total and Methylmercury Concentrations in Samples Collected in October 1987 at the Whitlingham Sewage Treatment Works

Location	Average TotHg Conc. (ng/l)	Average MeHg Conc. [(a)] (ng/l)	MeHg Conc. Range (ng/l)	Number of MeHg Samples	Number of MeHg Results below the MDL [(a)]
Raw Sewage	200	11	< MDL - 83	11	9
Settled Sewage	100	<10	all < MDL	11	11
Picket Fence Thickener Overflow	300	23	16 - 36	5	0
Returned Activated Sludge	5900	120	68 - 200	4	0
Final Effluent	100	<10	< MDL - 20	13	7

[(a)] The method detection limit was 10 ng/l. The average concentrations were calculated by the study authors assuming that values below the detection limit were zero.

Table 11: Methylmercury Data Excluded from Calculations in this Report

NPDES #	Facility	Sample Date	Sample Location	MeHg Conc (ng/l)
CA0083861	Aerojet Interim GW WTP	11/18/05	EFF1	ND (<0.025)
CA0083861	Aerojet Interim GW WTP	11/18/05	EFF2	ND (<0.025)
CA0083861	Aerojet Interim GW WTP	11/18/05	EFF3	ND (<0.025)
CA0083861	Aerojet Interim GW WTP	11/18/05	EFF4	ND (<0.025)
CA0004111	Aerojet Sacramento Facility	3/18/05	EFF1	0.057
CA0004995	Corning Industries/ Domestic WWTP	9/22/04	EFF1	0.041
CA0078093	Deuel Vocational Institute WWTP	10/26/04	EFF1	ND (<0.02)
CA0078875	DGS Office of State Publishing	7/8/05	EFF1	ND (<0.02)
CA0078671	El Dorado Hills WWTP	8/9/05	EFF1	0.057
CA0078671	El Dorado Hills WWTP	8/9/05	INF1	1.41
CA0081833	General Electric Co. GWCS	10/8/04	EFF1	0.131
CA0081833	General Electric Co. GWCS	10/8/04	EFF2	0.184
CA0081833	General Electric Co. GWCS	10/8/04	EFF3	0.158
CA0081833	General Electric Co. GWCS	10/8/04	INF1	1.112
CA0081833	General Electric Co. GWCS	10/8/04	INF2	1.112
CA0081833	General Electric Co. GWCS	10/8/04	INF3	1.112
CA0084476	Lincoln WWTP	8/25/05	EFF1	0.034
CA0083801	Modesto ID Regional WTP	10/8/04	EFF1	0.038
CA0083801	Modesto ID Regional WTP	10/8/04	INF1	ND (<0.02)
CA0083143	South Feather Water & Power Agency Miners Ranch WTP	9/9/04	EFF1	ND (<0.025)
CA0078794	SRCSD Walnut Grove WWTP (CSD1)	12/29/04	EFF1	0.759
CA0078794	SRCSD Walnut Grove WWTP (CSD1)	12/29/04	INF1	1.15

Table 12: Relative Percent Differences (RPD) of Field Duplicate Samples Analyzed for Methylmercury

Sample Date	NPDES #	Facility Name	[MeHg] (ng/l)		RPD[(a)]
			Duplicate 1	Duplicate 2	
11/16/04	CA0004791	DFG Mokelumne River Fish Hatchery	< 0.020	< 0.020	---
2/4/04	CA0004863	Mirant Delta CCPP	0.084	0.080	4.9
3/3/04	CA0004863	Mirant Delta CCPP	0.120	0.122	1.7
3/8/05	CA0077691	Vacaville Easterly WWTP	0.057	0.055	3.6
8/18/04	CA0078956	Placerville Hangtown Creek WWTP	0.097	0.067	36.6
9/20/04	CA0078956	Placerville Hangtown Creek WWTP	0.063	0.043	37.7
4/28/05	CA0078956	Placerville Hangtown Creek WWTP	0.040	0.040	0.0
8/18/04	CA0079138	Stockton WWTP	1.290	1.380	6.7
9/8/04	CA0079138	Stockton WWTP	0.904	0.903	0.1
10/13/04	CA0079138	Stockton WWTP	0.392	0.384	2.1
11/10/04	CA0079138	Stockton WWTP	0.518	0.515	0.6
12/15/04	CA0079138	Stockton WWTP	1.640	1.830	11.0
1/19/05	CA0079138	Stockton WWTP	1.860	1.490	22.1
2/8/05	CA0079138	Stockton WWTP	2.090	2.080	0.5
3/9/05	CA0079138	Stockton WWTP	1.470	1.480	0.7
4/6/05	CA0079138	Stockton WWTP	0.627	0.703	11.4
5/10/05	CA0079138	Stockton WWTP	0.281	0.261	7.4
6/8/05	CA0079138	Stockton WWTP	< 0.020	< 0.020	---
7/6/05	CA0079138	Stockton WWTP	0.142	0.070	67.9
8/24/04	CA0079260	Yuba City WWTP	0.036	0.038	5.4
10/12/04	CA0079260	Yuba City WWTP	0.042	0.032	27.0
11/22/04	CA0079260	Yuba City WWTP	0.051	0.043	17.0
12/7/04	CA0079260	Yuba City WWTP	0.038	0.041	7.6
1/25/05	CA0079260	Yuba City WWTP	0.047	0.055	15.7
2/8/05	CA0079260	Yuba City WWTP	0.219	0.225	2.7
3/30/05	CA0079260	Yuba City WWTP	0.053	0.068	24.8
4/25/05	CA0079260	Yuba City WWTP	0.057	0.061	6.8
5/26/05	CA0079260	Yuba City WWTP	0.084	0.099	16.4
6/14/05	CA0079260	Yuba City WWTP	0.050	0.048	4.1
7/5/05	CA0079260	Yuba City WWTP	< 0.025	< 0.025	---
1/24/05	CA0081833	General Electric Co. GWCS	< 0.020	< 0.020	---
4/18/05	CA0081833	General Electric Co. GWCS	< 0.020	< 0.020	---
7/5/05	CA0081833	General Electric Co. GWCS	< 0.020	< 0.020	---
12/8/04	CA0081931	Defense Logistics Agency Sharpe GW Cleanup	0.022	< 0.020	---
6/6/06	CA0083861	Aerojet Interim GW WTP	< 0.025	< 0.025	---

[(a)] RPD = |(Duplicate 1 - Duplicate 2)| / ((Duplicate 1 + Duplicate 2)/2) x 100. The RPD was not calculated if one or both samples were reported as below the method detection limit (MDL). Mean RPD = 12.7.

Table 13: Anomalous Values Observed in the Methylmercury and Total Mercury Data

NPDES No.	Facility	Sample Date(s)	Value(s) (ng/l)	Range of values of all other data (ng/l)
Influent Methylmercury				
CA0079898	Grass Valley WWTP	11/4/2004	5.01	0.588 - 3.00
CA0077895	UC Davis WWTP	9/22/2004	11.1	0.074 - 4.92
CA0077950	Woodland WWTP	6/14/2005	7.07	0.767 - 3.94
Effluent Methylmercury				
CA0079049	Davis WWTP (Discharge 2)	6/7/2005	1.44	0.247 - 0.556
CA0078590	Discovery Bay WWTP	10/27/2004	2.03	ND - 0.059
CA0079243	Lodi White Slough WWTP	4/13/2005	1.24	ND - 0.063
CA0079898	Grass Valley WWTP	7/7/2005, 8/4/2005	0.932, 0.938	ND - 0.128
Influent Total Mercury				
CA0084573	Roseville Pleasant Grove WWTP	6/1/2005, 5/26/2005	590, 770	29.0 - 200
CA0079243	Lodi White Slough WWTP	11/9/2004	590	41.0 - 270
CA0079502	Roseville Dry Creek WWTP	10/25/2004	910	46.0 - 290
CA0077682	SRCSD Sacramento River WWTP	3/11/2004, 1/6/2004	3400, 6100	48.5 - 1280
Effluent Total Mercury				
CA0079103	Modesto WWTP	12/29/2004	19	ND - 6.50
CA0079731	Redding Clear Creek WWTP	10/18/2004	23.3	1.37 - 3.01
CA0077682	SRCSD Sacramento River WWTP	11/3/2004	29.5	2.40 - 20.0
CA0077950	Woodland WWTP	12/9/2004	53.1	0.91 - 2.98
CA0079367	Placer Co. SMD #3 WWTP	6/1/2005	7.97	0.88 - 3.12
CA0082589	Redding Stillwater WWTP	3/17/2005	6.19	0.92 - 3.25
CA0084573	Roseville Pleasant Grove WWTP	8/30/2004	3	0.70 - 1.80

Table 14: Sum of Annual Average Daily Discharges (mgd) for Facilities within Each Discharger Type for NPDES Facilities in the Delta Source Region [a]

Facility Type	Proximity to Delta		TOTAL	% of TOTAL
	Delta / Yolo Bypass	Downstream of Major Dam		
Aggregate & Lake Dewatering	9.2	3.9	**13.1**	**1.8%**
Aquaculture		256.5	**256.5**	**34.6%**
Drinking Water Treatment		1.0	**1.0**	**0.1%**
Food Processing		1.7	**1.7**	**0.2%**
Groundwater Remediation		10.5	**10.5**	**1.4%**
Heating/Cooling	5.3	0.02	**5.3**	**0.7%**
Mines		0.1	**0.1**	**0.01%**
Miscellaneous [b]		0.4	**0.4**	**0.05%**
Municipal WWTP	214.6	112.5	**326**	**44.1%**
Paper & Saw Mills		2.6	**2.6**	**0.4%**
Power Generation	124.0	0.02	**124.0**	**16.7%**
Total	**353.0**	**389.2**	**742.3**	**100%**

[a] The average daily discharges of the facilities in the Delta source region were calculated using information available in NPDES permits and monitoring reports, updated in September 2009 because several manufacturing, drinking water treatment, and municipal WWTP facilities recently ceased to discharge to surface waters.

[b] The "Miscellaneous" category includes publishing and laboratory facilities.

Table 15: Number of NPDES Facilities That Received the 13267 Order Categorized by Facility Type and Geographical Region

Facility Type	Proximity to Delta			TOTAL
	Delta / Yolo Bypass	Downstream of Major Dam	Upstream of Major Dam	
Aggregate & Lake Dewatering	1	4		**5**
Aquaculture		12	2	**14**
Drinking Water Treatment		7		**7**
Food Processing		4		**4**
Groundwater Remediation		7		**7**
Heating/Cooling	3	2	1	**6**
Landfill		1		**1**
Manufacturing		2		**2**
Mines			2	**2**
Miscellaneous [a]		3		**3**
Municipal WWTP	16	41	12	**69**
Paper/Saw Mills		4	1	**5**
Power Generation	2	6		**8**
Power Generation/ Domestic WWTP		1		**1**
Grand Total	**22**	**94**	**18**	**134**

[a] The "Miscellaneous" category includes publishing and laboratory facilities.

Table 16: NPDES Facility Receiving Water Information and Map Labels for Figures 1 through 3

NPDES No.	Facility	Facility Type	Annual Discharge (mgd)	Receiving Water	Discharges to 303(d) Hg Listed Waterway	LATITUDE (North)	LONGITUDE (West)	Map Code
CA0083861	Aerojet Interim Groundwater Treatment Plant	Groundwater Remediation	5.00	Buffalo Ck. / American R.	No	38.616667	-121.242777	60
CA0004111	Aerojet Sacramento Facility	Heating / Cooling	0.02	Buffalo Ck. / American R.	No	38.621	-121.2311	59
CA0077704	Anderson WWTP	Mun WWTP	1.40	Sacramento R.	No	40.468889	-122.279167	14
CA0079197	Atwater WWTP	Mun WWTP	3.40	Atwater Drain / Bear Ck. / San Joaquin R.	No	37.341111	-120.605556	108
CA0077712	Auburn WWTP	Mun WWTP	1.17	Auburn Ravine / East Side Canal / Cross Canal / Sacramento R.	No	38.8895	-121.1007	47
CA0083721	Bell Carter Olive Company Inc.	Food Processing	0.38	Sacramento R.	No	39.913889	-122.091667	23
CA0080799	Bella Vista Water District	Drinking Water Treatment	0.50	Boulder Ck. / Churn Ck. / Sacramento R.	No	40.6001	-122.3466	9
CA0078930	Biggs WWTP	Mun WWTP	0.38	Main Drainage Canal (near Biggs) / Butte Ck. / Sacramento R.	No	39.4072	-121.7241	28
CA0084891	Boeing Company Interim Groundwater Treatment System	Groundwater Remediation	0.56	drainage ditch on Mather Field / Morrison Ck. / Stone Lake / Sacramento R.	No [c]	38.56875	-121.302278	64
CA0082660	Brentwood WWTP	Mun WWTP	3.09	Marsh Ck.	Yes	37.960278	-121.69	88
CA0082082	CA Dairies, Inc. Los Banos Foods [b]	Food Processing	0.50	municipal storm drain / San Luis Canal / Mud Slough and Salt Slough / San Joaquin R.	No	37.0563	-120.8368	112
CA0078581	CA State of, Central Heating/Cooling Facility [b]	Heating / Cooling	5.26	Sacramento R.	Yes	38.573889	-121.51	63
CA0083968	CALAMCO - Stockton Terminal [b]	Heating / Cooling	5.06	Wine Slip portion of the Deep Water Channel in the Port of Stockton / San Joaquin R.	Yes	37.941389	-121.325	89
CA0081752	Calaveras Trout Farm (Rearing Facility)	Aquaculture	19.40	Merced R. / San Joaquin R.	Yes	37.5156	-120.3747	105
CA0081566	Calpine Corp. Greenleaf Unit One Cogen Plant [b]	Power Generation	0.11	unnamed trib / North Drain / E Sutter Bypass	No	39.043889	-121.674167	40

Table 16: NPDES Facility Receiving Water Information and Map Labels for Figures 1 through 3

NPDES No.	Facility	Facility Type	Annual Discharge (mgd)	Receiving Water	Discharges to 303(d) Hg Listed Waterway	LATITUDE (North)	LONGITUDE (West)	Map Code
CA0082040	Camanche Dam Powerhouse [b]	Power Generation	0.04	Mokelumne R.	No	38.22	-121.025278	80
CA0083682	Canada Cove LP French Camp Golf & RV Park	Mun WWTP	0.04	Lone Tree Ck. / Little Johns Ck. / French Camp Slough / San Joaquin R.	No [c]	37.874167	-121.225	93
CA0079081	Chico Regional WWTP	Mun WWTP	7.20	Sacramento R.	Yes	39.7	-121.95	25
CA0083828	Clear Creek CSD WTP	Drinking Water Treatment	0.16	Clear Ck. / Sacramento R.	No	40.597222	-122.538056	10
CA0079529	Colfax WWTP [a]	Mun WWTP	0.024	Smuthers Ravine / Bunch Canyon / N Fk. American R.	No	39.075	-120.941667	38
CA0078999	Colusa WWTP	Mun WWTP	0.66	Powell Slough / Colusa Basin Drain / Sacramento R.	No	39.180556	-122.03	35
CA0004995	Corning Industries/ Domestic WWTP	Mun WWTP	1.00	Sacramento R.	No	39.913889	-122.091667	22
CA0081507	Cottonwood WWTP	Mun WWTP	0.29	Cottonwood Ck. / Sacramento R.	No	40.377778	-122.270833	18
CA0082767	Crystal Creek Aggregate	Aggregate	0.002	Rock Ck. & Middle Ck. / Sacramento R.	No	40.609	-122.4601	8
CA0079049	Davis WWTP [d]	Mun WWTP	5.26	Willow Slough Bypass / Yolo Bypass	No [c]	38.59	-121.663889	62
CA0081931	Defense Logistics Agency Sharpe Groundwater Cleanup [b]	Groundwater Remediation	1.90	South San Joaquin Irrigation District Canal / French Camp Slough / San Joaquin R.	No [c]	37.8405	-121.2622	95
CA0078093	Deuel Vocational Institute WWTP	Mun WWTP	0.47	Deuel Drain / Paradise Cut / Old R.	Yes	37.750556	-121.326389	101
CA0004561	DFG Darrah Springs Fish Hatchery	Aquaculture	18.70	Baldwin Ck. / Battle Ck. / Sacramento R.	No	40.4329	-121.9967	15
CA0080055	DFG Merced River Fish Hatchery	Aquaculture	4.55	Merced R. / San Joaquin R.	Yes	37.5172	-120.372	104
CA0004804	DFG Moccasin Creek Fish Hatchery [a]	Aquaculture	19.62	Moccasin Ck. / Don Pedro Res.	No	37.8136	-120.3063	96

Table 16: NPDES Facility Receiving Water Information and Map Labels for Figures 1 through 3

NPDES No.	Facility	Facility Type	Annual Discharge (mgd)	Receiving Water	Discharges to 303(d) Hg Listed Waterway	LATITUDE (North)	LONGITUDE (West)	Map Code
CA0004791	DFG Mokelumne River Fish Hatchery	Aquaculture	21.00	Mokelumne R.	No	38.2254	-121.0306	79
CA0004774	DFG Nimbus Fish Hatchery	Aquaculture	40.00	American R.	Yes	38.6341	-121.2286	57
CA0004812	DFG San Joaquin Fish Hatchery	Aquaculture	22.60	San Joaquin R.	No	36.997222	-119.718889	113
CA0078875	DGS Office of State Publishing	Misc	0.30	American R.	Yes	38.602	-121.4941	61
CA0078590	Discovery Bay WWTP	Mun WWTP	1.54	Reclamation District 800 drainage ditch / Old R.	Yes	37.905556	-121.5875	92
CA0078662	El Dorado ID Deer Creek WWTP	Mun WWTP	2.52	Deer Ck. / Cosumnes R.	No	38.628333	-120.986389	58
CA0078671	El Dorado ID El Dorado Hills WWTP	Mun WWTP	1.08	Carson Ck. / Deer Ck. / Cosumnes R.	No	38.638333	-121.060556	56
CA0004057	Formica Corporation Sierra Plant [b]	Manufacturing	0.88	Unnamed trib. / Pleasant Grove Ck. / Cross Canal / Sacramento R.	No	38.8232	-121.3077	49
CA0081434	Galt WWTP	Mun WWTP	1.92	Laguna Ck. / Cosumnes R.	No	38.297222	-121.333333	77
CA0004847	Gaylord Container Corp. Antioch Pulp & Paper Mill [b]	Heating / Cooling	- - -	San Joaquin R.	Yes	38.025833	-121.7675	85
CA0081833	General Electric Co. GWCS	Groundwater Remediation	1.60	Doane Lateral Irrigation Canal (Merced Irrigation District) / Miles Ck. / San Joaquin R.	No	37.2918	-120.4234	109
CA0079898	Grass Valley WWTP [a]	Mun WWTP	2.10	Wolf Ck. / Indian Ck. / Bear R.	No	39.208333	-121.07	34
CA0082309	GWF Power Systems	Power Generation	0.05	Storm Drain / San Joaquin R.	Yes	38.025	-121.758333	86
CA0004146	Hershey Chocolate USA, Oakdale	Food Processing	1.03	Oakdale Irrigation District Riverbank Lateral Canal / Modesto Irrigation District Main Canal / Stanislaus R.	No	37.758333	-120.829722	100
CA0083097	J.F. Shea C Fawndale Rock and Asphalt	Aggregate	3.87	W. Fk. Stillwater Ck. / Stillwater Ck. / Sacramento R.	No	40.735	-122.307222	1

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NPDES No.	Facility	Facility Type	Annual Discharge (mgd)	Receiving Water	Discharges to 303(d) Hg Listed Waterway	LATITUDE (North)	LONGITUDE (West)	Map Code
CA0079391	Jackson WWTP [a]	Mun WWTP	0.71	Jackson Ck. / Dry Ck. / Mokelumne R.	No	38.344722	-120.783611	72
CA0081191	Lehigh Southwest Cement Co.	Aggregate		W Fk. Stillwater Ck. / Stillwater Ck. / Sacramento R.	No	40.733889	-122.320833	2
CA0084476	Lincoln WWTP	Mun WWTP	1.13	Auburn Ravine / East Side Canal / Cross Canal / Sacramento R.	No	38.891111	-121.324722	46
CA0079022	Live Oak WWTP	Mun WWTP	1.65	Reclamation District No. 777 Lateral Drain No. 1 / Main Canal / Sutter Bypass	No	39.258333	-121.677222	32
CA0079243	Lodi White Slough WWTP	Mun WWTP	4.51	Dredger Cut / White Slough	Yes	38.093056	-121.396667	84
CA0082783	Manteca Aggregate Sand Plant (Oakwood Lake Subdivision Mining Reclamation)	Aggregate	9.15	San Joaquin R.	Yes	37.7794	-121.2993	98
CA0081558	Manteca WWTP	Mun WWTP	4.63	San Joaquin R.	Yes	37.7794	-121.2993	99
CA0079430	Mariposa PUD WWTP	Mun WWTP	0.245	Mariposa Ck. several miles u/s of Mariposa Ck. Dam	No	37.480278	-119.960833	106
CA0079987	Maxwell PUD WWTP	Mun WWTP	0.14	unnamed trib / Laurline Ck. / Colusa Basin Drain / Sacramento R.	No	39.266667	-122.183333	29
CA0079219	Merced WWTP	Mun WWTP	8.50	Hartley Slough / Owens Ck. / Bear Ck. / San Joaquin R.	No	37.243889	-120.541667	111
CA0004863	Mirant Delta CCPP	Power Generation	124	San Joaquin R.	Yes	38.019444	-121.7625	87
CA0083801	Modesto ID Regional WTP [b]	Drinking Water Treatment	0.04	Modesto Irrigation Main Canal / Stanislaus R. / Tuolumne R. / San Joaquin R.	No	37.653611	-120.6725	102
CA0079103	Modesto WWTP	Mun WWTP	11.8	San Joaquin R.	Yes	37.521944	-121.099444	103
CA0079901	Nevada City WWTP	Mun WWTP	0.43	Deer Ck. / Yuba R.	No	39.25975	-121.03075	31
CA0083241	Nevada Co SD #1 Cascade Shores WWTP [a]	Mun WWTP	0.026	Gas Canyon Ck. / Greenhorn Ck. / Rollins Res. / Bear R.	No	39.261111	-120.905556	30

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NPDES No.	Facility	Facility Type	Annual Discharge (mgd)	Receiving Water	Discharges to 303(d) Hg Listed Waterway	LATITUDE (North)	LONGITUDE (West)	Map Code
CA0077828	Nevada Co SD #1 Lake Wildwood WWTP [a]	Mun WWTP	0.50	Deer Ck. / Yuba R.	No	39.233333	-121.222778	33
CA0081612	Nevada Co SD #2 Lake of the Pines WWTP [a]	Mun WWTP	0.54	Magnolia Ck. / Bear R.	No	39.033333	-121.083611	41
CA0077836	Olivehurst PUD WWTP	Mun WWTP	1.20	Western Pacific Interceptor Drainage Canal / Bear R. / Feather R.	No	39.065278	-121.552222	39
CA0079235	Oroville WWTP	Mun WWTP	3.00	Feather R.	Yes	39.453056	-121.636944	27
CA0082961	Pacific Coast Sprout Farms, Inc. (Sacramento Facility)	Aquaculture	0.10	Morrison Ck.	No [c]	38.5197	-121.3789	70
CA0004821	Pactiv Molded Pulp Mill	Paper/Saw Mill	1.90	Sacramento R.	No	40.1553	-122.2095	21
CA0083488	Paradise Irrigation District	Drinking Water Treatment	1.5	Magalia Reservoir / Little Butte Ck. / Butte Ck. / Sacramento R.	No	39.816389	-121.580556	24
CA0079341	Placer Co. SA #28 Zone #6 [b]	Mun WWTP	0.01	Drainage Ditch / Yankee Slough / Bear R.	No	38.9754	-121.3709	42
CA0079316	Placer Co. SMD #1 WWTP	Mun WWTP	1.90	Coon Ck. / Main Canal / Cross Canal / Sacramento R.	No	38.958333	-121.116667	43
CA0079367	Placer Co. SMD #3 WWTP	Mun WWTP	0.12	Miners Ravine / Dry Ck. / Natomas East Main Drainage Canal / Bannon Slough / Sacramento R.	No	38.797222	-121.118056	50
CA0078956	Placerville Hangtown Creek WWTP [a]	Mun WWTP	1.30	Hangtown Ck. / Weber Ck. / S. Fk. American R. / Folsom Lake / American R.	No	38.733333	-120.841667	52
CA0078950	Planada Comm. Service Dist. WWTP	Mun WWTP	0.38	Miles Ck. / Owens Ck. / Bear Ck. / San Joaquin R.	No	37.276389	-120.333333	110
CA0004316	Proctor & Gamble Co. WWTP [b]	Manufacturing	5.50	Morrison Ck.	No [c]	38.5315	-121.4088	65
CA0078891	Red Bluff WWRP	Mun WWTP	1.40	Sacramento R.	No	40.1625	-122.216667	20
CA0079731	Redding Clear Creek WWTP	Mun WWTP	7.50	Sacramento R.	No	40.498889	-122.360278	11

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NPDES No.	Facility	Facility Type	Annual Discharge (mgd)	Receiving Water	Discharges to 303(d) Hg Listed Waterway	LATITUDE (North)	LONGITUDE (West)	Map Code
CA0082589	Redding Stillwater WWTP	Mun WWTP	3.46	Sacramento R.	No	40.473611	-122.267222	13
CA0077852	Rio Alto WD- Lake CA WWTP	Mun WWTP	0.15	Sacramento R.	No	40.3319	-122.2101	19
CA0079588	Rio Vista Main WWTP	Mun WWTP	0.47	Sacramento R.	Yes	38.154167	-121.677778	82
CA0079502	Roseville Dry Creek WWTP	Mun WWTP	13.0	Dry Ck. / Natomas East Main Drainage Canal / Bannon Slough / Sacramento R.	No	38.731389	-121.316111	53
CA0084573	Roseville Pleasant Grove WWTP	Mun WWTP	4.82	Pleasant Grove Ck. / Pleasant Grove Ck. Canal / Cross Canal / Sacramento R.	No	38.795556	-121.379444	51
CA0083569	Sacramento Cogen Authority Procter & Gamble Plant [b]	Power Generation	- - -	Morrison Ck.	No [c]	38.530278	-121.4075	66
CA0034841	Sacramento International Airport [b]	Heating / Cooling	1.50	Lindbergh ditch / Meister canal / Reclamation District-1000 pump station / Sacramento R.	Yes	38.665833	-121.612778	55
CA0079464	San Andreas SD WWTP [a]	Mun WWTP	0.30	San Andreas Ck. / Murray Ck. / N Fk. Calaveras R.	No	38.203056	-120.688333	81
CA0082848	San Joaquin Co DPW – Flag City [b]	Mun WWTP	0.06	Highline Canal / White Slough, East of I-5	Yes	38.106944	-121.41	83
CA0004693	Shasta Lake WTP	Drinking Water Treatment	0.05	Churn Ck. / Sacramento R.	No	40.6929	-122.4025	4
CA0079511	Shasta Lake WWTP	Mun WWTP	0.64	Churn Ck. / Sacramento R.	No	40.661111	-122.375	6
CA0004758	SMUD Rancho Seco Nuclear Generating Station [b]	Power / Dom WWTP	0.09	Clay to Hadselville to Laguna Ck. / Cosumnes R.	No	38.343056	-121.126111	76
CA0083143	South Feather Water and Power	Drinking Water Treatment	0.25	Miners Ranch Res. / Feather R.	No	39.504722	-121.456389	26
CA0082066	SPI Anderson Division	Paper/Saw Mill		Sacramento R.	No	40.4787	-122.3231	12
CA0081400	SPI Shasta Lake	Paper/Saw Mill	0.15	unnamed trib / Churn Ck. / Sacramento R.	No	40.675278	-122.384722	5
CA0077682	SRCSD Sacramento River WWTP	Mun WWTP	151	Sacramento R.	Yes	38.4607	-121.5031	73

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NPDES No.	Facility	Facility Type	Annual Discharge (mgd)	Receiving Water	Discharges to 303(d) Hg Listed Waterway	LATITUDE (North)	LONGITUDE (West)	Map Code
CA0078794	SRCSD Walnut Grove WWTP (CSD1) [b]	Mun WWTP	0.08	unnamed agricultural ditch / Snodgrass Slough / Mokelumne R. / San Joaquin R.	Yes	38.2344	-121.4998	78
CA0084140	Stimpel Wiebelhaus Associates SWA at Mountain Gate	Aggregate	0.02	Stillwater Ck. / Sacramento R.	No	40.636944	-122.32	7
CA0081965	Stockton Cogen Co. [b]	Power Generation	1.17	North Little Johns Ck. / French Camp Slough / San Joaquin R.	No [c]	37.853889	-121.259722	94
CA0079138	Stockton WWTP	Mun WWTP	27.78	San Joaquin R.	Yes	37.9375	-121.334722	90
CA0079154	Tracy WWTP	Mun WWTP	9.49	Old R. / Middle R. / San Joaquin R.	Yes	37.801944	-121.400833	97
CA0084727	Tuolumne UD Sonora WWTP / Jamestown WWTP [a]	Mun WWTP	0.16	Woods Ck. / Slate Ck. / Don Pedro Res	No	37.922222	-120.431389	91
CA0078948	Turlock WWTP	Mun WWTP	11.71	Harding Drain / San Joaquin R.	Yes	37.463333	-121.031667	107
CA0083551	UA Local 38 Trust Fund Konocti Harbor Resort and Spa [a]	Heating / Cooling	0.22	Clear Lake	Yes	38.9405	-122.7378	45
CA0083348	UC Davis Center for Aquatic Biology & Aquaculture – Putah Ck Facility	Aquaculture	0.14	South Fk. Putah Ck. / Yolo Bypass	Yes	38.5275	-121.805	67
CA0083348	UC Davis Center for Aquatic Biology & Aquaculture – Aquatic Center	Aquaculture	0.67	South Fk. Putah Ck. / Yolo Bypass	Yes	38.525556	-121.788889	69
CA0084182	UC Davis Hydraulics Laboratory	Misc	0.01	North Fk. Putah Ck. / Putah Ck. / Yolo Bypass	No [c]	38.526389	-121.781944	68
CA0077895	UC Davis WWTP	Mun WWTP	1.92	South Fk. Putah Ck. / Yolo Bypass	Yes	38.517778	-121.756944	71
CA0084697	United Auburn Indian Community Casino WWTP	Mun WWTP	0.15	Unnamed trib. / Orchard Ck. / Auburn Ravine / East Side Canal / Cross Canal / Sacramento R.	No	38.841667	-121.316667	48
CA0084905	USDI BR Sliger Mine [a]	Mines	0.06	Middle Fk. American R.	No	38.940994	-120.932769	44

Table 16: NPDES Facility Receiving Water Information and Map Labels for Figures 1 through 3

NPDES No.	Facility	Facility Type	Annual Discharge (mgd)	Receiving Water	Discharges to 303(d) Hg Listed Waterway	LATITUDE (North)	LONGITUDE (West)	Map Code
CA0084298	USDI BR Winter Run Rearing Facility (Livingston Stone) [a]	Aquaculture	1.00	Sacramento R.	No	40.716667	-122.423889	3
CA0004201	USDI FWS Coleman Fish Hatchery	Aquaculture	40.08	Battle Ck. / Sacramento R.	No	40.3981	-122.1438	17
CA0077691	Vacaville Easterly WWTP	Mun WWTP	9.26	Old Alamo Ck. / Ulatis Ck.	No [c]	38.347222	-121.910278	75
CA0079171	West Sacramento WWTP [b]	Mun WWTP	5.60	Sacramento R.	Yes	38.436111	-121.526111	74
CA0081957	Wheelabrator Shasta Energy Co.	Power Generation	0.02	Anderson Cottonwood Canal / Cottonwood Ck.	No	40.430278	-122.275556	16
CA0077933	Williams WWTP	Mun WWTP	0.44	Salt Ck. / Glenn-Colusa Canal / Colusa Basin Drain / Sacramento R.	No	39.169722	-122.153611	36
CA0077950	Woodland WWTP	Mun WWTP	6.05	Tule Canal / Yolo Bypass	No [c]	38.680833	-121.643889	54
CA0079260	Yuba City WWTP	Mun WWTP	5.22	Feather R.	Yes	39.090556	-121.598056	37

[a] Facilities upstream of a major dam.
[b] Facilities for which NPDES permits were rescinded sometime after the facilities completed 13267 Order monitoring.
[c] Facilities that do not discharge to 303(d) Listed mercury-impaired waterways but do discharge to small tributaries that drain directly to the Delta.
[d] The City of Davis WWTP (CA0079049) has two seasonal discharge locations; wastewater is discharged from Discharge 001 to the Willow Slough Bypass upstream of the Yolo Bypass and from Discharge 002 to the Conaway Ranch Toe Drain in the Yolo Bypass. The latitude and longitude coordinates and other information provided in the table are for Discharge 001. The coordinates for Discharge 002 are 38.575833, -121.633889.

Table 17: Summary of all Effluent Methylmercury Concentration Data for the Non-Municipal Facility Categories [a]

Facility Type	# of Effluent MeHg Samples	Average MeHg Conc (ng/l) [b]	# of Nondetect samples	MeHg Conc. Range (ng/l)
Aggregate	10	0.026	7	ND - 0.081
Aquaculture	38	0.041	12	ND - 0.243
Drinking Water Treatment	10	0.033	3	ND - 0.066
Food Processing	12	0.014	9	ND - 0.027
Groundwater Remediation	20	0.012	19	ND - 0.033
Heating/Cooling	14	0.110	3	ND - 0.919
Manufacturing	5	0.023	3	ND - 0.050
Mines	4	0.064	1	ND - 0.091
Miscellaneous	6	0.034	3	ND - 0.082
Paper/Saw Mills	21	0.117	5	ND - 1.190
Power Generation	46	0.061	11	ND - 0.178
Power Generation/ Domestic WWTP	12	0.040	4	ND – 0.104

[a] This table summarizes all of the effluent methylmercury data submitted by non-municipal facilities including multiple discharge locations (e.g., effluents 1-4).

[b] One-half of the MDL was used in calculations for methylmercury concentration results that were less than the MDL.

Table 18: Available Intake and Outfall Methylmercury Concentration Data for Aquaculture, Power and Heating/Cooling Facilities in the Delta Region

Facility [NPDES #, Type]	Sample Date	Outfall 1 MeHg Conc. [(a)] (ng/l)	Outfall 1 MeHg Qual. [(b)]	Outfall 2 MeHg Conc. (ng/l)	Outfall 2 MeHg Qual. [(b)]	Outfall 2 Field Dup. MeHg Conc. (ng/l)	Outfall 2 Field Dup. MeHg Qual. [(b)]	Intake 1 MeHg Conc. [(a)] (ng/l)	Intake 1 MeHg Qual. [(b)]	Intake 1 Dup. MeHg Conc. (ng/l)	Intake 1 Dup. MeHg Qual. [(b)]	Intake 2 MeHg Conc. (ng/l)	Intake 2 MeHg Qual. [(b)]
CALAMCO - Stockton Terminal [CA0083968, Heating /Cooling]	8/26/2004	0.03	B					0.026	B				
Calaveras Trout Farm (Rearing Facility) [CA0081752, Aquaculture]	9/30/2004	0.027	B					0.067					
Camanche Dam Powerhouse [CA0082040, Power Generation]	1/19/2005	ND	<MDL					0.095	(ba)				
DFG Darrah Springs Fish Hatchery [CA0004561, Aquaculture]	9/15/2004	0.029	B, (nn)	0.043	B, X, (mm)			ND	<MDL, (nn)			ND	<MDL, (nn)
DFG Mokelumne River Fish Hatchery [CA0004791, Aquaculture]	11/16/2004	0.048	A					ND	<MDL, A	ND	<MDL, A		
DFG Nimbus Fish Hatchery [CA0004774, Aquaculture]	11/16/2004			0.129	A			0.051	A				
	2/17/2005	0.053										0.031	
	6/20/2005	0.085	A					0.052					
DFG San Joaquin Fish Hatchery [CA0004812, Aquaculture]	9/28/2004	0.073						0.021	B				
GWF Power Systems [CA0082309, Power Generation]	8/11/2004	ND	<MDL					ND	<MDL				
	11/4/2004	ND	<MDL					ND	<MDL				
	2/3/2005	ND	<MDL					0.263					
	5/5/2005	ND	<MDL					ND	<MDL				
Mirant Delta CCPP [CA0004863, Power Generation]	2/4/2004	0.081		0.0835		0.0799		0.296	(l)				
	3/3/2004	0.116		0.127				0.12	(l)	0.122	(l)		
	8/3/2004	0.020	J	0.07				ND	<MDL, (l)				
	9/1/2004	0.08		0.06				0.08	(l)				
	10/5/2004	0.049	B	0.06				0.038	(l), B				
	11/2/2004	0.047	B	0.042	B			0.04	(l), B				
	12/2/2004	0.03	B	0.063				0.07	(l)				

Table 18: Available Intake and Outfall Methylmercury Concentration Data for Aquaculture, Power and Heating/Cooling Facilities in the Delta Region

Facility [NPDES #, Type]	Sample Date	Outfall 1 MeHg Conc. [(a)] (ng/l)	Outfall 1 MeHg Qual. [(b)]	Outfall 2 MeHg Conc. (ng/l)	Outfall 2 MeHg Qual. [(b)]	Outfall 2 Field Dup. MeHg Conc. (ng/l)	Outfall 2 Field Dup. MeHg Qual. [(b)]	Intake 1 MeHg Conc. [(a)] (ng/l)	Intake 1 MeHg Qual. [(b)]	Intake 1 Dup. MeHg Conc. (ng/l)	Intake 1 Dup. MeHg Qual. [(b)]	Intake 2 MeHg Conc. (ng/l)	Intake 2 MeHg Qual. [(b)]
Mirant Delta CCPP [CA0004863, Power Generation]	1/11/2005	0.083		0.081				0.102	(l)				
	2/8/2005	0.097		0.12				0.098	(l)				
	3/8/2005	0.121		0.15				0.15	(l)				
	4/26/2005	0.083			Y			0.069	(l)				
	5/25/2005	0.091			Y			0.077	(l)				
Sacramento Cogen Authority Procter & Gamble Plant [CA0083569, Power Generation]	8/11/2004	0.056	A					ND	<MDL, A				
	10/6/2004	0.069						ND	<MDL				
	1/5/2005	0.07						0.08					
	5/4/2005	ND	<MDL					ND	<MDL				

[(a)] ND: nondetect (below method detection limit). Analytical method detection limits were 0.025 ng/l or less.
[(b)] < MDL: below method detection limit
A: Samples were received out of optimal temperature range.
B: Sample results above the MDL and below the ML; should be considered an estimate.
J: Detected but below the reporting limit; result is an estimated concentration.
X: Collected 9/14/04.
Y: No discharge.
(l): Mirant Delta CCPP Intake 002.
(mm): Darrah Springs Fish Hatchery - Lower Springs.
(nn): Darrah Springs Fish Hatchery - Upper Springs.
(ba): Camanche Dam Powerhouse receiving water received 200 feet upstream of discharge.

Table 19: Comparison of Delta Municipal WWTP Effluent Methylmercury Concentrations to Methylmercury Concentrations in Drinking Water Supplies for Delta Communities

Municipal Area	Municipal WWTP Average MeHg Conc. in Effluent Discharged to Surface Water (ng/l)	Municipal Water Supply [a]				Local Surface Drinking Water Supply [b]	
		Central Valley Project	State Water Project	Ground-water [m]	Local Streams / Reservoirs	Sampling Location	Average MeHg Conc. (ng/l)
Brentwood	0.01		X	X		SWP	0.054
Deuel Vocational Institute [c]	0.01			X		- - -	- - -
Discovery Bay [d]	0.19			X	X	CVP SWP X2	0.064 0.054 0.083
Lodi White Slough	0.15			X		- - -	- - -
Manteca [e]	0.22			X		- - -	- - -
Modesto [n]							
Rio Vista [f]	0.16			X		- - -	- - -
San Joaquin Co DPW CSA 31 Flag City [g]	0.08			X		- - -	- - -
SRCSD Sacramento River [l]	0.73			X	X	Sacramento R. @ Freeport American River	0.103 0.045
SRCSD Walnut Grove [h]	2.16			X		- - -	---
Stockton [j]	0.94			X	X	*No MeHg data available for New Hogan & New Melones Reservoirs*	
Tracy [e, i]	0.15	X		X	X	CVP Stanislaus River	0.064 0.119
West Sacramento [k]	0.05	X			X	Sacramento R. @ Veterans Bridge CVP	0.109 0.064
Woodland	0.03			X		- - -	---

Table 19 Footnotes:

[a] Except where otherwise noted, all water supply information was obtained from the Water Education Foundation's 2006 website, "Where does my water come from?" [http://www.water-ed.org/watersources/]. This site lists the drinking water sources for incorporated cities with a population of 10,000 or greater, as determined from the 2005 Water Education Foundation survey, water agencies, and annual water quality reports.

[b] If methylmercury data were not available for the local surface water supply, data for nearby waterways were included. Methylmercury data for the Central Valley Project (CVP), State Water Project (SWP) and Delta outflows to San Francisco Bay (X2) were used to represent drinking water intakes in the Central and West Delta, such as the Rock Slough and Old River intakes for the Randall-Bold Water Treatment Plant located in Oakley (see footnote "d"). Average methylmercury values were obtained from the February 2008 Delta TMDL draft staff report (Wood *et al.*, 2008b) for all surface water locations with four exceptions. Central Valley Water Board staff collected methylmercury samples from the American River at Discovery Park and Stanislaus River at Caswell State Park as part of a broader CalFed-funded study (Foe *et al.*, 2007; 2008 draft report in peer review). The Sacramento Coordinated Monitoring Program sampled the Sacramento River at Veteran's Bridge (CMP, 2004).

[c] The Deuel Vocational Institute WWTP services the Deuel Vocational Institute (DVI), which is about two miles south of Mossdale and ten miles south of Stockton. Information about its water supply was obtained from a case study described in: Corrollo Engineers, 2007, Drinking Water with Emphasis on Desalination and Membrane Softening Qualifications, available at: http://www.carollo.com/356/section.aspx/333

[d] Groundwater from eight active wells provides approximately 67% of the Discovery Bay water supply; the remaining water comes from the Randall-Bold Water Treatment Plant located in Oakley, which is jointly owned by Contra Costa Water District (CCWD) and Diablo Water District (DWD) and receives water from Rock Slough, Old River, and Los Vaqueros Reservoir. Information about the Discovery Bay water supply is from: Brown and Caldwell, 2006. City of Brentwood 2005 Urban Water Management Plan - Final. Prepared for the City of Brentwood by Department of Public Works by Brown and Caldwell, Walnut Creek, California. January 2006. Available at: http://www.ci.brentwood.ca.us/pdf/new/publicworks/2005_urban_water_plan.pdf

[e] The Water Education Foundation listed Manteca water sources as both groundwater and local streams/reservoirs. The City of Manteca Water Division website [http://www.ci.manteca.ca.us/eng/water/] stated that as of 2005, 100% of the Manteca drinking water supply came from groundwater sources and that in the near future some of its supply will come from the South County Surface Water Supply Project, which will draw water from Woodward Reservoir. The Woodward Reservoir is supplied by the Stanislaus River. The South County Surface Water Supply Project is a project to supply the cities of Tracy, Lathrop, Manteca and Escalon with water from the South San Joaquin Irrigation District and includes construction of a new water treatment plant at Woodward Reservoir and pipelines to supply water to the cities. Currently no methylmercury data are available for Woodward Reservoir.

[f] The City of Rio Vista relies on groundwater sources and has the right to obtain a specified amount of North Bay Aqueduct (NBA, a component of the State Water Project) water in the future, but as of 2003, had no facility to take NBA water. [Information from: Solano County Water Agency, 2002. SWCA Briefing Book. January 2002. Available at: http://www.scwa2.com/briefing_book.html]

[g] County Service Area 31 is an 80-acre parcel that includes Flag City, a collection of hotels, gas stations and restaurants at Interstate 5 and Highway 12 near Lodi.

[h] Per California American Water's 2005 Annual Water Quality Report for Walnut Grove [PWS ID: 3410047], water in the Walnut Grove system comes from wells that pump groundwater from aquifers in the Walnut Grove area. [Report available at: http://www.illinoisamerican.com/awpr1/caaw/pdf/CA-WalnutGrove-web.pdf]

Table 19 Footnotes, *continued*:

[i] According to the City of Tracy Public Works website, 2005 sources of the City of Tracy's water supply include the Delta-Mendota Canal [a.k.a. Central Valley Project] (50%), the Stanislaus River (17%), and groundwater pumped from wells (33%). [http://www.ci.tracy.ca.us/departments/public_works/water_quality/]

[j] In 2005, the City of Stockton obtained about 58% of their drinking water from surface water supplied by the Stockton East Water District (SEWD) and 42% from groundwater sources [City of Stockton / OMI Thames Water 2005 Annual Drinking Water Quality Report, California Water System No. 3910012.] SEWD obtains water from the New Hogan Reservoir in the Calaveras River watershed, and from the New Melones Reservoir in the Stanislaus River watershed. [Report available at: http://www.stocktongov.com/MUD/General/water/documents/2005CCRWaterQualityReport.pdf] Currently no methylmercury data are available for the reservoirs.

[k] The West Sacramento 2006 Water Quality Consumer Confidence Report states that the City of West Sacramento's main water supply is the Sacramento River, with an intake structure at Bryte Bend, upstream of the confluence of the Sacramento and American rivers. The City maintains water supply contracts with the federal Bureau of Reclamation, the Central Valley Project and the North Delta Water Agency. In addition to surface water, the City has five ground water wells that are available to supply additional water during emergencies. The City did not utilize ground water in 2005.

[l] The 2005 City of Sacramento Water Quality Report states that 85% of its water supply comes from the American and Sacramento Rivers and 15% comes from groundwater. [Report available at: http://www.cityofsacramento.org/utilities/pubs/DOU_CCR_2005.pdf] According to the November 2006 City of Sacramento Urban Water Management Plan prepared by West Yost Associates, the City diverts water from the American River downstream from the Howe Avenue Bridge, and from the Sacramento River downstream of the confluence of the American and Sacramento Rivers. [Report available at: http://www.cityofsacramento.org/utilities/urbanwater/] According to available water quality reports for urban areas outside of the City of Sacramento serviced by other water districts and private corporations, water supply for unincorporated areas is a mixture of surface water (e.g., Sacramento River, American River, and Folsom Lake) and groundwater. The effluent methylmercury data used in this analysis was collected from December 2000 to June 2003, since the surface drinking water supply data was collected during the same time period.

[m] Groundwater treatment plant intake and discharge monitoring (Tables B.1 through B.4) indicate that methylmercury concentrations in groundwater are at or below method detection limits (typically < 0.02 ng/l).

[n] The Modesto Irrigation District (ID) Water Treatment Plant (WTP), which supplements groundwater drinking water supplies for the Modesto community, obtains water from the Tuolumne River at Modesto Reservoir. The Modesto ID collected intake samples and analyzed them for methylmercury as part of their 13267 Order monitoring effort (see Table B.3). Modesto ID WTP water supply information is available at: http://www.mid.org/water/drnkwtr.htm

Table 20: Municipal WWTP Treatment Processes in Place at the Time of Methylmercury Sampling

Agency (NPDES No.)	Ave EFF1 MeHg Conc (ng/l) [a]	Title 22 [b]	1. Primary Clarification	2. Activated Sludge	3. Pure Oxygen Act. Sludge	4. RBC's [c]	5. SBR's [c]	6. Fixed Film Reactors	7. Trickling Filters	8. Extended Aeration	9. Settling Ponds	10. Oxidation Ditch	11. Oxidation Ponds	12. Facultative Ponds	13. Lemna/Overland Flow	14. Nitrify / Denitrify	15. Secondary Clarification	16. Dissolved Air Flotation	17. Coagulation / Polymer	18. Microfiltration	19. Filtration	20. Chlorination	21. Chlorination / Dechlor.	22. Ultraviolet Radiation	23. Ozonation	Average Flow (mgd)	Design Maximum Flow (mgd) [e]	Systems in Place during MeHg 13267 sampling [d]
Brentwood WWTP (CA0082660)	0.010	X	X							X		X				X	X		X		X	X				3.1	4.5	Y
Deuel Vocational Institute WWTP (CA0078093)	0.010											X				X	X				X	X				0.47	0.62	Y
United Auburn Indian Comm. Casino WWTP (CA0084697)	0.010	X		X												X	X			X				X		0.15	0.35	Y
Redding Stillwater WWTP (CA0082589)	0.013			X																	X		X			3.5	4.0	Y
El Dorado ID Deer Creek WWTP (CA0078662)	0.015	X	X	X						X		X				X					X		X			2.5	2.5	Y
Roseville Pleasant Grove WWTP (CA0084573)	0.017	X		X								X				X	X		X		X		X			4.8	12	Y
El Dorado ID El Dorado Hills WWTP (CA0078671)	0.018	X	X	X												X		X			X	X				1.1	3.0	Y
Lincoln WWTP (CA0084476)	0.018	X										X				X		X	X		X			X		1.1	3.3	Y
Shasta Lake WWTP (CA0079511)	0.022											X					X				X		X			0.64	1.3	Y
Roseville Dry Creek WWTP (CA0079502)	0.023	X	X	X												X	X		X		X		X			13	18	Y
Vacaville Easterly WWTP (CA0077691)	0.024		X	X													X						X			9.3	10	Y
Red Bluff WWTP (CA0078891)	0.027		X	X													X				X		X			1.4	2.5	Y
Auburn WWTP (CA0077712)	0.028	X										X				X	X		X		X		X			1.2	1.67	Y
Woodland WWTP (CA0077950)	0.031	X										X					X						X			6.1	7.8	Y
Atwater WWTP (CA0079197)	0.034		X	X													X						X			3.4	6.0	N?
UC Davis WWTP (CA0077895)	0.038	X										X				X	X				X			X		1.9	2.7	Y
Redding Clear Creek WWTP (CA0079731)	0.042		X	X													X				X		X			7.5	8.8	Y
Corning Industries/ Domestic WWTP (CA0004995)	0.044											X					X						X			1.0	1.38	Y
Nevada City WWTP (CA0079901)	0.048	X					X														X		X			0.43	0.69	Y
West Sacramento WWTP (CA0079171)	0.050		X	X												X	X						X			5.6	7.5	Y
Placerville Hangtown Creek WWTP (CA0078956)	0.058	X	X	X					X								X				X		X			1.3	2.3	Y
Turlock WWTP (CA0078948)	0.059			X													X						X			11.71	20	Y
San Joaquin Co DPW - Flag City WWTP (CA0082848)	0.081									X							X				X		X			0.06	0.16	Y

Table 20: Municipal WWTP Treatment Processes in Place at the Time of Methylmercury Sampling

Agency (NPDES No.)	Ave EFF1 MeHg Conc (ng/l) [a]	Title 22 [b]	1. Primary Clarification	2. Activated Sludge	3. Pure Oxygen Act. Sludge	4. RBC's [c]	5. SBR's [c]	6. Fixed Film Reactors	7. Trickling Filters	8. Extended Aeration	9. Settling Ponds	10. Oxidation Ditch	11. Oxidation Ponds	12. Facultative Ponds	13. Lemna/Overland Flow	14. Nitrify / Denitrify	15. Secondary Clarification	16. Dissolved Air Flotation	17. Coagulation / Polymer	18. Microfiltration	19. Filtration	20. Chlorination	21. Chlorination / Dechlor.	22. Ultraviolet Radiation	23. Ozonation	Average Flow (mgd)	Design Maximum Flow (mgd) [e]	Systems in Place during MeHg 13267 sampling [d]
Anderson WWTP (CA0077704)	0.090			X													X				X		X			1.4	2.0	Y
Cottonwood WWTP (CA0081507)	0.096											X					X				X		X			0.29	0.43	Y
Placer Co. SMD #3 WWTP (CA0079367)	0.100		X						X								X		X		X		X			0.12	0.3	Y
Jackson WWTP (CA0079391)	0.108	X										X					X				X		X			0.71	0.71	Y
Nevada Co SD #1 Lake Wildwood WWTP (CA0077828)	0.109											X					X				X		X			0.50	1.1	Y*
Chico Regional WWTP (CA0079081)	0.126		X	X						X							X					X				7.2	9.0	Y
Lodi White Slough WWTP (CA0079243)	0.128		X	X													X				X			X		4.5	7.0	Y
Modesto WWTP (CA0079103)	0.130		X					X						X									X			7.2	70	Y
Galt WWTP (CA0081434)	0.139			X						X							X						X			1.9	3.0	Y**
Placer Co. SMD #1 WWTP (CA0079316)	0.141	X	X			X			X								X				X		X			1.90	2.18	Y
Nevada Co SD #1 Cascade Shores WWTP (CA0083241)	0.142	X		X													X				X		X			0.026	0.03	Y
Olivehurst PUD WWTP (CA0077836)	0.144	X	X	X													X						X			1.2	1.8	Y***
Tracy WWTP (CA0079154)	0.145		X	X					X								X						X			9.5	9 *upgrade to 16*	Y****
Canada Cove LP French Camp WWTP (CA0083682)	0.147						X										X				X				X	0.04	0.04	Y
Oroville WWTP (CA0079235)	0.147		X	X													X				X		X			3.0	6.5	Y
Grass Valley WWTP (CA0079898)	0.160	X	X	X												X	X						X			2.1	2.78	Y
Rio Vista Main WWTP (CA0079588)	0.164		X	X													X						X			0.47	0.65	Y
Tuolumne UD Sonora WWTP/ Jamestown WWTP (CA0084727)	0.182		X						X								X					X				0.16	2.6	Y
Discovery Bay WWTP (CA0078590)	0.191											X				X	X							X		1.5	2.1	Y
Colfax WWTP (CA0079529)	0.197	X												X									X			0.024	0.16	Y
Manteca WWTP (CA0081558)	0.216		X	X													X						X			4.6	8.11	Y***
San Andreas SD WWTP (CA0079464)	0.249		X						X								X						X			0.3	0.4	Y

Table 20: Municipal WWTP Treatment Processes in Place at the Time of Methylmercury Sampling

Agency (NPDES No.)	Ave EFF1 MeHg Conc (ng/l) [a]	Title 22 [b]	1. Primary Clarification	2. Activated Sludge	3. Pure Oxygen Act. Sludge	4. RBC's [c]	5. SBR's [c]	6. Fixed Film Reactors	7. Trickling Filters	8. Extended Aeration	9. Settling Ponds	10. Oxidation Ditch	11. Oxidation Ponds	12. Facultative Ponds	13. Lemna/Overland Flow	14. Nitrify / Denitrify	15. Secondary Clarification	16. Dissolved Air Flotation	17. Coagulation / Polymer	18. Microfiltration	19. Filtration	20. Chlorination	21. Chlorination / Dechlor.	22. Ultraviolet Radiation	23. Ozonation	Average Flow (mgd)	Design Maximum Flow (mgd) [e]	Systems in Place during MeHg 13267 sampling [d]
Yuba City WWTP (CA0079260)	0.295		X		X												X						X			5.22	7.0	Y
Merced WWTP (CA0079219)	0.386		X	X													X						X			8.5	10	Y
Mariposa PUD WWTP (CA0079430)	0.393											X					X						X			0.25	0.61	Y
Davis WWTP (CA0079049)	0.546	X	X										X		X								X			5.3	7.5	Y****
Live Oak WWTP (CA0079022)	0.591	X												X									X			1.65	1.6 / 5.9	Y
SRCSD Sacramento River WWTP (CA0077682)	0.613		X		X												X						X			151	181	Y
Placer Co. SA #28 Zone #6 WWTP (CA0079341)	0.668	X									X			X								X				0.01	0.1	Y
Stockton WWTP (CA0079138)	0.935		X						X				X								X		X			28	55	Y
Maxwell PUD WWTP (CA0079987)	0.993	X											X									X				0.14	0.2	Y****
Planada Comm. Service Dist. WWTP (CA0078950)	1.168										X			X							X	X				0.38	0.38	Y
Nevada Co SD #2 Lake of the Pines WWTP (CA0081612)	1.409	X												X			X		X		X		X			0.54	0.72	Y***
Williams WWTP (CA0077933)	1.553	X												X									X			0.44	0.5	Y****
Biggs WWTP (CA0078930)	1.605								X		X			X									X			0.38	0.53	Y
Rio Alto WD- Lake CA WWTP (CA0077852)	1.746											X					X				X		X			0.15	0.64	Y
SRCSD Walnut Grove WWTP (CSD1) (CA0078794)	2.155										X		X										X			0.08	0.5	Y
Colusa WWTP (CA0078999)	2.863	X									X				X								X			0.66	0.9	Y

[a] One-half of the method detection limit (MDL) was used in calculations for methylmercury concentration results that were less than the MDL.

[b] The California Department of Public Health (DPH) has developed reclamation criteria (CCR, Division 4, Chapter 3 (Title 22)) for the reuse of wastewater. Title 22 requires that for spray irrigation of food crops, parks, playgrounds, schoolyards, and other areas of similar public access, wastewater be adequately disinfected, oxidized, coagulated, clarified, and filtered, and that the effluent total coliform levels not exceed 2.2 MPN/100 mL as a 7-day median. The regulatory criteria include numerical limitations and requirements, treatment method requirements, and provisions and requirements related to sampling and analysis, engineering reports, design, operation, maintenance and reliability of facilities.

[c] RBC's: Rotating Biological Contactors SBR's: Sequencing Batch Reactors

[d] *Tertiary, no Title 22. ** No tertiary. *** No Title 22. **** No tertiary, no Title 22.

[e] If two values are provided, the first is design average dry weather flow and the second is design peak wet weather flow.

Table 21: Treatment Categories and Effluent Methylmercury Descriptive Statistics for the Municipal WWTPs

NPDES No.	WWTP	2005 Treatment Category [(a)]	# of Samples	# of Non-detect Samples	Average MeHg Conc. (ng/l)	Median MeHg Conc. (ng/l)	MeHg Conc. Range (ng/l)	Std. Deviation (ng/l)	Coefficient of Variation (%)
CA0077704	Anderson	Filtration + Chlor./ Dechlor.	12	2	0.090	0.067	ND - 0.271	0.084	93
CA0079197	Atwater	Secondary + Chlor./ Dechlor.	12	3	0.034	0.033	ND - 0.084	0.021	62
CA0077712	Auburn	N/D + Filtration + Chlor./ Dechlor.	12	6	0.028	0.023	ND - 0.072	0.021	75
CA0078930	Biggs	Pond + Chlor./ Dechlor.	2	0	1.605	1.605	0.150 - 3.060	2.058	128
CA0082660	Brentwood	N/D + Filtration + Chlor./ Dechlor.	13	13	*(all sample results < MDL)*				
CA0083682	Canada Cove LP French Camp	Filtration + Ozonation	4	0	0.147	0.134	0.029 - 0.291	0.127	86
CA0079081	Chico Regional	Secondary + Chlor./ Dechlor.	12	0	0.126	0.118	0.057 - 0.178	0.035	28
CA0079529	Colfax	Pond + Chlor./ Dechlor.	3	0	0.197	0.126	0.115 - 0.350	0.133	67
CA0078999	Colusa	Pond + Chlor./ Dechlor.	4	0	2.863	2.730	1.970 - 4.020	0.924	32
CA0004995	Corning Industries/ Domestic	Secondary + Chlor./ Dechlor.	2	0	0.044	0.044	0.034 - 0.053	0.013	31
CA0081507	Cottonwood	Filtration + Chlor./ Dechlor.	5	0	0.096	0.047	0.045 - 0.245	0.086	90
CA0079049	Davis (Discharge 1)	Pond + Chlor./ Dechlor.	7	0	0.546	0.533	0.305 - 1.040	0.252	46
CA0079049	Davis (Discharge 2)	Pond + Chlor./ Dechlor.	5	0	0.613	0.514	0.247 - 1.440	0.481	78
CA0078662	Deer Creek	N/D + Filtration + Chlor./ Dechlor.	13	11	0.015	0.013	ND - 0.032	0.006	41
CA0078093	Deuel Vocational Institute	Filtration + Chlor./ Dechlor.	3	3	*(all sample results < MDL)*				
CA0078590	Discovery Bay	Secondary w/ N/D + UV	12	7	0.191	0.013	ND - 2.030	0.579	303
CA0078671	El Dorado Hills (Discharge 1)	N/D + Filtration + Chlor./ Dechlor.	12	10	0.018	0.013	ND - 0.055	0.014	76
CA0078671	El Dorado Hills (Discharge 2)	N/D + Filtration + Chlor./ Dechlor.	2	2	*(all sample results < MDL)*				
CA0081434	Galt	Secondary + Chlor./ Dechlor.	6	0	0.139	0.142	0.027 - 0.220	0.068	49
CA0079898	Grass Valley	Secondary w/ N/D + Chlor./ Dechlor.	16	2	0.160	0.030	ND - 0.938	0.305	190
CA0079391	Jackson	Filtration + Chlor./ Dechlor.	4	0	0.108	0.104	0.061 - 0.161	0.041	38
CA0084476	Lincoln	N/D + Filtration + UV	7	6	0.018	0.010	ND - 0.068	0.022	120

Table 21: Treatment Categories and Effluent Methylmercury Descriptive Statistics for the Municipal WWTPs

NPDES No.	WWTP	2005 Treatment Category [(a)]	# of Samples	# of Non-detect Samples	Average MeHg Conc. (ng/l)	Median MeHg Conc. (ng/l)	MeHg Conc. Range (ng/l)	Std. Deviation (ng/l)	Coefficient of Variation (%)
CA0079022	Live Oak	Pond + Chlor./ Dechlor.	4	0	0.591	0.575	0.427 - 0.785	0.152	26
CA0079243	Lodi White Slough	Filtration + UV	12	4	0.128	0.025	ND - 1.240	0.351	275
CA0081558	Manteca	Secondary + Chlor./ Dechlor.	11	0	0.216	0.229	0.037 - 0.356	0.082	38
CA0079430	Mariposa PUD	Secondary + Chlor./ Dechlor.	4	0	0.393	0.309	0.040 - 0.912	0.417	106
CA0079987	Maxwell PUD	Pond + Chlor./ Dechlor.	4	0	0.993	1.104	0.044 - 1.720	0.849	86
CA0079219	Merced	Secondary + Chlor./ Dechlor.	12	0	0.386	0.369	0.130 - 0.672	0.156	40
CA0079103	Modesto	Pond + Chlor./ Dechlor.	9	0	0.130	0.118	0.108 - 0.170	0.025	19
CA0079901	Nevada City	Filtration + Chlor./ Dechlor.	4	2	0.048	0.018	ND - 0.146	0.066	137
CA0083241	Nevada Co SD #1 Cascade Shores	Filtration + Chlor./ Dechlor.	3	1	0.142	0.131	ND - 0.286	0.138	97
CA0077828	Nevada Co SD #1 Lake Wildwood	Filtration + Chlor./ Dechlor.	12	1	0.109	0.086	ND - 0.320	0.084	77
CA0081612	Nevada Co SD #2 Lake of the Pines	Pond + Filtration + Chlor./ Dechlor.	2	0	1.409	1.409	0.708 - 2.110	0.991	70
CA0077836	Olivehurst PUD	Secondary + Chlor./ Dechlor.	13	1	0.144	0.121	ND - 0.268	0.094	65
CA0079235	Oroville	Filtration + Chlor./ Dechlor.	12	0	0.147	0.148	0.061 - 0.280	0.072	49
CA0079341	Placer Co. SA #28 Zone #6	Pond + Chlor./ Dechlor.	2	0	0.668	0.668	0.474 - 0.862	0.274	41
CA0079316	Placer Co. SMD #1	Filtration + Chlor./ Dechlor.	12	0	0.141	0.142	0.042 - 0.350	0.092	65
CA0079367	Placer Co. SMD #3	Filtration + Chlor./ Dechlor.	12	0	0.100	0.069	0.037 - 0.381	0.095	95
CA0078956	Placerville Hangtown Creek	Filtration + Chlor./ Dechlor.	12	1	0.058	0.044	ND - 0.170	0.041	69
CA0078950	Planada Comm. Service Dist.	Pond + Filtration + Chlor./ Dechlor.	4	0	1.168	1.128	0.374 - 2.040	0.885	76
CA0078891	Red Bluff	Filtration + Chlor./ Dechlor.	12	6	0.027	0.025	ND - 0.057	0.018	67
CA0079731	Redding Clear Creek	Filtration + Chlor./ Dechlor.	12	3	0.042	0.039	ND - 0.084	0.024	57
CA0082589	Redding Stillwater	Filtration + Chlor./ Dechlor.	12	12	*(all sample results < MDL)*				
CA0077852	Rio Alto WD- Lake CA	Filtration + Chlor./ Dechlor.	2	0	1.746	1.746	0.141 - 3.350	2.269	130
CA0079588	Rio Vista Main	Secondary + Chlor./ Dechlor.	4	0	0.164	0.049	0.035 - 0.522	0.239	146
CA0079502	Roseville Dry Creek	N/D + Filtration + Chlor./ Dechlor.	12	4	0.023	0.021	ND - 0.055	0.014	60

Table 21: Treatment Categories and Effluent Methylmercury Descriptive Statistics for the Municipal WWTPs

NPDES No.	WWTP	2005 Treatment Category [a]	# of Samples	# of Non-detect Samples	Average MeHg Conc. (ng/l)	Median MeHg Conc. (ng/l)	MeHg Conc. Range (ng/l)	Std. Deviation (ng/l)	Coefficient of Variation (%)
CA0084573	Roseville Pleasant Grove	N/D + Filtration + Chlor./ Dechlor.	12	10	0.017	0.010	ND - 0.070	0.018	107
CA0079464	San Andreas SD	Secondary + Chlor./ Dechlor.	4	0	0.249	0.262	0.178 - 0.293	0.053	21
CA0082848	San Joaquin Co DPW - Flag City	Filtration + Chlor./ Dechlor.	3	1	0.081	0.078	ND - 0.152	0.070	86
CA0079511	Shasta Lake	Filtration + Chlor./ Dechlor.	2	1	0.022	0.022	ND - 0.034	0.017	77
CA0077682	SRCSD Sacramento River	Secondary + Chlor./ Dechlor.	108	0	0.613	0.551	0.118 - 1.640	0.336	55
CA0078794	SRCSD Walnut Grove	Pond + Chlor./ Dechlor.	2	0	2.155	2.155	0.949 - 3.36	1.705	79
CA0079138	Stockton	Pond + Filtration + Chlor./ Dechlor.	12	1	0.935	0.766	ND - 2.090	0.712	76
CA0079154	Tracy	Secondary + Chlor./ Dechlor.	13	1	0.145	0.132	ND - 0.422	0.104	72
CA0084727	Tuolumne UD Sonora / Jamestown	Secondary + Chlor./ Dechlor.	3	0	0.182	0.213	0.071 - 0.262	0.099	55
CA0078948	Turlock	Secondary + Chlor./ Dechlor.	12	1	0.059	0.062	ND - 0.079	0.019	32
CA0077895	UC Davis	N/D + Filtration + UV	12	3	0.038	0.030	ND - 0.078	0.025	65
CA0084697	United Auburn Indian Community Casino	N/D + Filtration + UV	2	2	*(all sample results < MDL)*				
CA0077691	Vacaville Easterly	Secondary + Chlor./ Dechlor.	12	4	0.024	0.024	ND - 0.057	0.014	57
CA0079171	West Sacramento	Secondary w/ N/D + Chlor./ Dechlor.	12	1	0.050	0.050	ND - 0.085	0.022	44
CA0077933	Williams	Pond + Chlor./ Dechlor.	4	0	1.553	1.775	0.560 - 2.100	0.691	45
CA0077950	Woodland	Secondary + Chlor./ Dechlor.	12	2	0.031	0.031	ND - 0.059	0.014	43
CA0079260	Yuba City	Secondary + Chlor./ Dechlor.	12	0	0.295	0.237	0.106 - 0.625	0.167	57

[a] Chlor./ Dechlor.: Chlorination and Dechlorination N/D: Nitrification/Denitrification UV: Ultraviolet radiation

Table 22: Description of Treatment Categories

2005 Treatment Category	Secondary Treatment	Nitrification/ Denitrification	Tertiary Treatment	Disinfection
Filtration + Chlor./ Dechlor.	Any	No	Yes	Chlorination/ Dechlorination
Filtration + Ozonation	Any	No	Yes	Ozonation
Filtration + UV	Any	No	Yes	Ultraviolet radiation
N/D + Filtration + Chlor./ Dechlor.	Any	Yes	Yes	Chlorination/ Dechlorination
N/D + Filtration + UV	Any	Yes	Yes	Ultraviolet radiation
Pond + Chlor./ Dechlor.	Treatment Pond (a)	No	No	Chlorination/ Dechlorination
Pond + Filtration + Chlor./ Dechlor.	Treatment Pond (a)	No	Yes	Chlorination/ Dechlorination
Secondary + Chlor./ Dechlor.	Any	No	No	Chlorination/ Dechlorination
Secondary w/ N/D + Chlor./ Dechlor.	Any	Yes	No	Chlorination/ Dechlorination
Secondary w/ N/D + UV	Any	Yes	No	Ultraviolet radiation

(a) The municipal WWTPs placed in the pond treatment categories use treatment pond systems (oxidation, facilitative, settling or stabilization ponds) as a significant part of their treatment process. These facilities may also use other types of secondary treatment in addition to the treatment ponds.

Table 23: Descriptive Statistics for the Effluent Methylmercury Concentrations for the Municipal WWTP Treatment Categories [a]

2005 Treatment Category	# of Facilities	# of samples	# of Non-detect samples	Ave. Effluent MeHg Conc. (ng/l)	Median Effluent MeHg Conc. (ng/l)	MeHg Conc. Range (ng/l)	Standard Error (ng/l) [b]	95% Conf. Interval (ng/l)	P_{25} (ng/l) [c]	P_{75} (ng/l) [d]	IQR (ng/l) [e]	g [f]	Shapiro-Wilk p-value [g]
Filtration + Chlor./ Dechlor.	17	134	33	0.105	0.056	ND - 3.350	0.025	0.050	0.025	0.113	0.088	10.39	<0.0001
Filtration + Ozonation	1	4	0	0.147	0.134	0.029 - 0.291	0.063	0.202	0.035	0.272	0.237	0.27	0.39
Filtration + UV	1	12	4	0.128	0.025	ND - 1.240	0.101	0.223	0.010	0.049	0.039	3.45	<0.00001
N/D + Filtration + Chlor./ Dechlor.	6	76	56	0.018	0.013	ND - 0.072	0.002	0.003	0.010	0.020	0.010	2.14	<0.00001
N/D + Filtration + UV	3	21	11	0.029	0.020	ND - 0.078	0.005	0.011	0.010	0.040	0.030	1.16	<0.001
Pond + Chlor./ Dechlor.	10	46	0	0.902	0.522	0.044 - 4.020	0.147	0.296	0.158	1.485	1.327	1.58	<0.00001
Pond + Filtration + Chlor./ Dechlor.	3	18	1	1.040	0.806	ND - 2.110	0.175	0.369	0.388	1.830	1.442	0.23	<0.05
Secondary + Chlor./ Dechlor.	17	252	12	0.351	0.243	ND - 1.640	0.021	0.042	0.076	0.537	0.461	1.39	<0.00001
Secondary w/ N/D + Chlor./ Dechlor.	2	28	3	0.113	0.045	ND - 0.938	0.044	0.091	0.028	0.085	0.057	3.41	<0.00001
Secondary w/ N/D + UV	1	12	7	0.191	0.013	ND - 2.030	0.167	0.368	0.013	0.050	0.037	3.99	<0.00001

[a] One-half of the MDL was used in calculations for methylmercury concentration results that were less than the MDL.
[b] The standard error is estimated standard deviation of the sample mean. It is calculated by dividing the sample standard deviation by the square root of the sample size.
[c] The 25th percentile (P_{25}) is a value which exceeds no more than 25 percent of the data and is exceeded by no more than 75 percent.
[d] The 75th percentile (P_{75}) is a value which exceeds no more than 75 percent of the data and is exceeded by no more than 25 percent.
[e] The interquartile range (IQR) is the 75th percentile minus the 25th percentile. The IQR is a measure of variability that is more resistant to outliers than the standard deviation.
[f] A positive coefficient of skewness (g) indicates that the distribution is right-skewed (i.e. the distribution is asymmetric with extreme values extending out longer to the right side or larger value side). Conversely, a negative coefficient of skewness indicates that the distribution is left-skewed. As the coefficient of skewness increases from zero in either the negative or positive direction, the more extreme the skewness of the distribution.
[g] If the Shapiro-Wilk W statistic is statistically significant (p-value is less than 0.05), then the hypothesis that the data distribution is normal is rejected. Therefore, a p-value less than 0.05 indicates that the distribution is most likely not normal.

Table 24: Kruskal-Wallis Multiple Comparison Results for Median Effluent Methylmercury Concentrations of the Treatment Categories

2005 Treatment Category [a]	Average Effluent MeHg Conc. (ng/l)	Median Effluent MeHg Conc. (ng/l)	Comparison p-values [b]								
			N/D + Filtration + Chlor./ Dechlor.	Secondary w/ N/D + UV	N/D + Filtration + UV	Filtration + UV	Secondary w/ N/D + Chlor./ Dechlor.	Filtration + Chlor./ Dechlor.	Secondary + Chlor./ Dechlor.	Pond + Chlor./ Dechlor.	Pond + Filtration + Chlor./ Dechlor.
N/D + Filtration + Chlor./ Dechlor.	0.018	0.013	--	1.0000	1.0000	1.0000	***0.0218***	***0.0000***	***0.0000***	***0.0000***	***0.0000***
Secondary w/ N/D + UV	0.191	0.013	1.0000	--	1.0000	1.0000	1.0000	1.0000	***0.0022***	***0.0000***	***0.0000***
N/D + Filtration + UV	0.029	0.020	1.0000	1.0000	--	1.0000	1.0000	0.2168	***0.0000***	***0.0000***	***0.0000***
Filtration + UV	0.128	0.025	1.0000	1.0000	1.0000	--	1.0000	1.0000	***0.0008***	***0.0000***	***0.0000***
Secondary w/ N/D + Chlor./ Dechlor.	0.113	0.045	***0.0218***	1.0000	1.0000	1.0000	--	1.0000	***0.0002***	***0.0000***	***0.0000***
Filtration + Chlor./ Dechlor.	0.105	0.056	***0.0000***	1.0000	0.2168	1.0000	1.0000	--	***0.0000***	***0.0000***	***0.0000***
Secondary + Chlor./ Dechlor.	0.351	0.243	***0.0000***	***0.0022***	***0.0000***	***0.0008***	***0.0002***	***0.0000***	--	***0.0488***	0.2101
Pond + Chlor./ Dechlor.	0.902	0.522	***0.0000***	***0.0000***	***0.0000***	***0.0000***	***0.0000***	***0.0000***	***0.0488***	--	1.0000
Pond + Filtration + Chlor./ Dechlor.	1.040	0.806	***0.0000***	***0.0000***	***0.0000***	***0.0000***	***0.0000***	***0.0000***	0.2101	1.0000	--

[a] Due to the small sample size and unusual treatment type, the "Filtration + Ozonation" treatment category was not included in this analysis.

[b] The comparison p-values between pairs were calculated with Statistica software. The p-values are two-sided significance levels multiplied by the number of possible combination pairs [k*(k-1)/2, where k is the total number of groups in the comparison]. The number of possible combination pairs in this comparison analysis is 36. P-values less than 0.05 are highlighted in ***bold and italics*** to identify statistically significant differences between treatment categories.

Table 25: Subcategories Based upon Secondary Treatment for the Municipal WWTPs

NPDES No.	WWTP	2005 Secondary Treatment Subcategory
Secondary + Chlor./ Dechlor.		
CA0079197	Atwater	Activated Sludge
CA0079081	Chico Regional	Activated Sludge
CA0004995	Corning Industries/ Domestic	Activated Sludge
CA0081434	Galt	Activated Sludge
CA0081558	Manteca	Activated Sludge
CA0079430	Mariposa PUD	Activated Sludge
CA0079219	Merced	Activated Sludge
CA0077836	Olivehurst PUD	Activated Sludge
CA0079588	Rio Vista Main	Activated Sludge
CA0079464	San Andreas SD	Fixed Media
CA0077682	SRCSD Sacramento River	Activated Sludge
CA0079154	Tracy	Activated Sludge + Trickling Filter
CA0084727	Tuolumne UD Sonora / Jamestown	Fixed Media
CA0078948	Turlock	Activated Sludge
CA0077691	Vacaville Easterly	Activated Sludge
CA0077950	Woodland	Activated Sludge
CA0079260	Yuba City	Activated Sludge
Filtration + Chlor./ Dechlor.		
CA0077704	Anderson	Activated Sludge
CA0081507	Cottonwood	Activated Sludge
CA0078093	Deuel Vocational Institute	Activated Sludge
CA0079391	Jackson	Activated Sludge
CA0079901	Nevada City	Activated Sludge
CA0083241	Nevada Co SD #1 Cascade Shores	Activated Sludge
CA0077828	Nevada Co SD #1 Lake Wildwood	Activated Sludge
CA0079235	Oroville	Activated Sludge
CA0079316	Placer Co. SMD #1	Fixed Media
CA0079367	Placer Co. SMD #3	Fixed Media
CA0078956	Placerville Hangtown Creek	Activated Sludge + Trickling Filter
CA0078891	Red Bluff	Activated Sludge
CA0079731	Redding Clear Creek	Activated Sludge
CA0082589	Redding Stillwater	Activated Sludge
CA0077852	Rio Alto WD- Lake CA	Activated Sludge
CA0082848	San Joaquin Co DPW - Flag City	Activated Sludge
CA0079511	Shasta Lake	Activated Sludge

Table 26: Descriptive Statistics for the Effluent Methylmercury Concentrations for the Municipal WWTP Subcategories [a]

2005 Secondary Treatment Subcategory	# of Facilities	# of samples	# of Non-detect samples	Ave. Effluent MeHg Conc. (ng/l)	Median Effluent MeHg Conc. (ng/l)	MeHg Conc. Range (ng/l)	Standard Error (ng/l) [b]	95% Conf. Interval (ng/l)	P_{25} (ng/l) [c]	P_{75} (ng/l) [d]	IQR (ng/l) [e]	g [f]	Shapiro-Wilk p-value [g]
Secondary + Chlor./ Dechlor.													
Activated Sludge	14	232	11	0.367	0.258	ND - 1.640	0.023	0.045	0.073	0.552	0.479	1.29	<0.00001
Activated Sludge + Trickling Filter	1	13	1	0.145	0.132	ND - 0.422	0.029	0.063	0.080	0.181	0.101	1.55	0.062
Fixed Media	2	7	0	0.220	0.239	0.071 - 0.293	0.029	0.071	0.178	0.285	0.107	-1.35	0.25
Filtration + Chlor./ Dechlor.													
Activated Sludge	14	98	32	0.107	0.048	ND - 3.350	0.034	0.068	0.013	0.100	0.087	9.20	<0.0001
Activated Sludge + Trickling Filter	1	12	1	0.058	0.044	ND - 0.170	0.012	0.026	0.039	0.062	0.023	2.14	<0.01
Fixed Media	2	24	0	0.121	0.078	0.037 - 0.381	0.019	0.040	0.050	0.151	0.101	1.64	<0.001

[a] One-half of the MDL was used in calculations for methylmercury concentration results that were less than the MDL.

[b] The standard error is estimated standard deviation of the sample mean. It is calculated by dividing the sample standard deviation by the square root of the sample size.

[c] The 25th percentile (P_{25}) is a value which exceeds no more than 25 percent of the data and is exceeded by no more than 75 percent.

[d] The 75th percentile (P_{75}) is a value which exceeds no more than 75 percent of the data and is exceeded by no more than 25 percent.

[e] The interquartile range (IQR) is the 75th percentile minus the 25th percentile. The IQR is a measure of variability that is more resistant to outliers than the standard deviation.

[f] A positive coefficient of skewness (g) indicates that the distribution is right-skewed (i.e. the distribution is asymmetric with extreme values extending out longer to the right side or larger value side). Conversely, a negative coefficient of skewness indicates that the distribution is left-skewed. As the coefficient of skewness increases from zero in either the negative or positive direction, the more extreme the skewness of the distribution.

[g] If the Shapiro-Wilk W statistic is statistically significant (p-value is less than 0.05), then the hypothesis that the data distribution is normal is rejected. Therefore, a p-value less than 0.05 indicates that the distribution is most likely not normal.

Table 27: Kruskal-Wallis Multiple Comparison Results for Median Effluent Methylmercury Concentrations of the Subcategories within the "Filtration + C/D" category

2005 Secondary Treatment Subcategory	Average (ng/l)	Median (ng/l)	Comparison p-values [(a)]		
			Activated Sludge + Trickling Filter	Activated Sludge	Fixed Media
Activated Sludge + Trickling Filter	0.058	0.044	--	1.0000	0.1556
Activated Sludge	0.107	0.048	1.0000	--	***0.0078***
Fixed Media	0.121	0.078	0.1556	***0.0078***	--

[(a)] The comparison p-values between pairs were calculated with Statistica software. The p-values are two-sided significance levels multiplied by the number of possible combination pairs [k*(k-1)/2, where k is the total number of groups in the comparison]. The number of possible combination pairs in this comparison analysis is 3. P-values less than 0.05 are highlighted in ***bold and italics*** to identify statistically significant differences between treatment categories.

Table 28: Two-sided Significance Levels (p-values) for WWTP Treatment Subcategories [(a)]

2005 Treatment Subcategory	Two sample t-test	Mann-Whitney U test
Activated Sludge	<0.0001 [(b)]	<0.0001
Activated Sludge + Trickling Filter	0.014 [(c)]	0.011
Fixed Media	0.015 [(c)]	0.009

[(a)] When comparing the same subcategory within the "Filtration + C/D" and "Secondary + C/D" categories.
[(b)] P-value for two sample t-test assuming equal variances.
[(c)] P-value for two sample t-test assuming unequal variances.

Table 29: Kruskal-Wallis Multiple Comparison Results for Median Effluent:Influent Methylmercury Ratios of the Treatment Categories

2005 Treatment Category [a]	Average Effluent:Influent MeHg Ratio	Median Effluent:Influent MeHg Ratio	Comparison p-values [b]						
			N/D + Filtration + Chlor./ Dechlor.	N/D + Filtration + UV	Filtration + Chlor./ Dechlor.	Filtration + UV	Secondary w/ N/D + Chlor./ Dechlor.	Secondary + Chlor./ Dechlor.	Pond + Chlor./ Dechlor.
N/D + Filtration + Chlor./ Dechlor.	2.4%	1.2%	--	1.0000	1.0000	1.0000	1.0000	***0.0000***	***0.0000***
N/D + Filtration + UV	2.7%	1.5%	1.0000	--	1.0000	1.0000	1.0000	***0.0000***	***0.0019***
Filtration + Chlor./ Dechlor.	4.1%	1.6%	1.0000	1.0000	--	1.0000	1.0000	***0.0109***	***0.0365***
Filtration + UV	6.0%	2.0%	1.0000	1.0000	1.0000	--	1.0000	***0.0004***	***0.0153***
Secondary w/ N/D + Chlor./ Dechlor.	10.2%	2.1%	1.0000	1.0000	1.0000	1.0000	--	***0.0006***	***0.0344***
Secondary + Chlor./ Dechlor.	36.8%	28.1%	***0.0000***	***0.0000***	***0.0109***	***0.0004***	***0.0006***	--	1.0000
Pond + Chlor./ Dechlor.	65.5%	36.4%	***0.0000***	***0.0019***	***0.0365***	***0.0153***	***0.0344***	1.0000	--

[a] The "Pond + Filtration + Chlor./ Dechlor." treatment category was not included in this analysis due to it having a sample size of one. Additionally, the "Secondary w/ N/D + UV" and "Filtration + Ozonation" treatment categories were not included since the facilities with these treatment types did not collect influent samples.

[b] The comparison p-values between pairs were calculated with Statistica software. The p-values are two-sided significance levels multiplied by the number of possible combination pairs [k*(k-1)/2, where k is the total number of groups in the comparison]. The number of possible combination pairs in this comparison analysis is 21. P-values less than 0.05 are highlighted in ***bold and italics*** to identify statistically significant differences between treatment categories.

Table 30: Regression Coefficients (R^2) and Two-sided Significance Levels (p-values) for Influent versus Effluent Methylmercury Concentration Scatter Plots for Each WWTP with Five or More Paired Data Points. [Significant relationships are in bold.]

NPDES #	WWTP	# of paired data points	R^2 value for linear regression	p-value for linear regression
CA0079081	Chico	11	0.026	0.636
CA0078662	Deer Creek	13	0.2374	0.091
CA0078671	El Dorado Hills (Discharge 1)	12	0.0832	0.363
CA0079898	Grass Valley	16	0.0092	0.724
CA0079243	**Lodi**	**12**	**0.4037**	**0.026**
CA0079502	Roseville Dry Creek	9	0.086	0.444
CA0084573	Roseville Pleasant Grove	9	0.02	0.717
CA0077682	**SRCSD Sacramento River**	**107**	**0.1739**	**0.000008**
CA0077895	**UC Davis**	**12**	**0.3875**	**0.031**
CA0077950	Woodland	12	0.0643	0.426

Table 31: Kruskal-Wallis Multiple Comparison Results for Median Effluent Methylmercury:Total Mercury Ratios of the Treatment Categories

2005 Treatment Category [a]	Average Effluent MeHg:THg Ratio	Median Effluent MeHg:THg Ratio	Comparison p-values [b]							
			Secondary w/ N/D + UV	N/D + Filtration + Chlor./ Dechlor.	Filtration + UV	Secondary w/ N/D + Chlor./ Dechlor.	Filtration + Chlor./ Dechlor.	Secondary + Chlor./ Dechlor.	Pond + Chlor./ Dechlor.	Pond + Filtration + Chlor./ Dechlor.
Secondary w/ N/D + UV	0.6%	0.5%	--	1.0000	1.0000	1.0000	***0.0415***	***0.0001***	***0.0002***	***0.0000***
N/D + Filtration + Chlor./ Dechlor.	1.2%	0.9%	1.0000	--	1.0000	1.0000	***0.0146***	***0.0000***	***0.0000***	***0.0000***
Filtration + UV	3.6%	1.0%	1.0000	1.0000	--	1.0000	1.0000	***0.0068***	***0.0095***	***0.0000***
Secondary w/ N/D + Chlor./ Dechlor.	1.8%	1.2%	1.0000	1.0000	1.0000	--	1.0000	0.1489	0.1196	***0.0002***
Filtration + Chlor./ Dechlor.	4.0%	2.9%	***0.0415***	***0.0146***	1.0000	1.0000	--	0.1234	0.3376	***0.0001***
Secondary + Chlor./ Dechlor.	6.7%	5.6%	***0.0001***	***0.0000***	***0.0068***	0.1489	0.1234	--	1.0000	***0.0225***
Pond + Chlor./ Dechlor.	11.0%	5.8%	***0.0002***	***0.0000***	***0.0095***	0.1196	0.3376	1.0000	--	0.7644
Pond + Filtration + Chlor./ Dechlor.	18.8%	16.9%	***0.0000***	***0.0000***	***0.0000***	***0.0002***	***0.0001***	***0.0225***	0.7644	--

[a] The "N/D + Filtration + UV" treatment category was not included in this analysis due to it having a sample size of one. Additionally, the "Filtration + Ozonation" treatment category was not included since the one facility with this treatment type did not collect influent samples.

[b] The comparison p-values between pairs were calculated with Statistica software. The p-values are two-sided significance levels multiplied by the number of possible combination pairs [k*(k-1)/2, where k is the total number of groups in the comparison]. The number of possible combination pairs in this comparison analysis is 36. P-values less than 0.05 are highlighted in ***bold and italics*** to identify statistically significant differences between treatment categories.

Table 32: Regression Coefficients (R^2) and Two-sided Significance Levels (p-values) for Inorganic Mercury versus Methylmercury Effluent Concentration Scatter Plots for Each WWTP with Five or More Paired Data Points. [Significant relationships are in bold.]

NPDES #	WWTP	# of paired data points	R^2 value for linear regression	p-value for linear regression
CA0082660	Brentwood	13	*all MeHg values are nondetect*	
CA0079049	**Davis (Discharges 1 & 2)**	**12**	**0.4445**	**0.018**
CA0078590	**Discovery Bay**	**9**	**0.551**	**0.022**
CA0079243	Lodi	12	0.0513	0.479
CA0081558	Manteca	11	0.2412	0.125
CA0079103	Modesto	9	0.0351	0.629
CA0079316	Placer Co. SMD #1	11	0.0383	0.564
CA0079367	Placer Co. SMD #3	12	0.0009	0.926
CA0079731	Redding Clear Creek	12	0.0055	0.819
CA0082589	Redding Stillwater	12	*all MeHg values are nondetect*	
CA0079502	Roseville Dry Creek	10	0.002	0.902
CA0084573	Roseville Pleasant Grove	11	0.0122	0.746
CA0077682	**SRCSD Sacramento River**	**106**	**0.0775**	**0.004**
CA0079138	**Stockton**	**12**	**0.67**	**0.001**
CA0079154	Tracy	13	0.0303	0.570
CA0078948	Turlock	12	0.0342	0.565
CA0077691	Vacaville Easterly	12	0.00009	0.977
CA0079171	West Sacramento	11	0.0161	0.710
CA0077950	Woodland	12	0.1906	0.156
CA0079260	Yuba City	12	0.1172	0.276

Table 33: Regression Coefficients (R^2) and Two-sided Significance Levels (p-values) for Influent Inorganic Mercury versus Effluent Methylmercury Concentration Scatter Plots for Each WWTP with Five or More Paired Data Points.

NPDES #	WWTP	# of paired data points	R^2 value for linear regression	p-value for linear regression
CA0079243	Lodi	12	0.0121	0.734
CA0079502	Roseville Dry Creek	9	0.1328	0.335
CA0084573	Roseville Pleasant Grove	9	0.1079	0.388
CA0077682	SRCSD Sacramento River	73	0.0017	0.729
CA0077950	Woodland	6	0.1403	0.464

Table 34: Regression Coefficients (R^2) and Two-sided Significance Levels (p-values) for Influent versus Effluent Inorganic Mercury Concentration Scatter Plots for Each WWTP with Five or More Paired Data Points

NPDES #	WWTP	# of paired data points	R^2 value for linear regression	p-value for linear regression
CA0079243	Lodi	12	0.1257	0.258
CA0079502	Roseville Dry Creek	9	0.0036	0.878
CA0084573	Roseville Pleasant Grove	9	0.1029	0.400
CA0077682	SRCSD Sacramento River	228	0.0004	0.764
CA0077950	Woodland	6	0.0117	0.838

Table 35: Sum of Annual Total Mercury Loads (g/yr) Discharged by Facilities within Each Discharger Category for NPDES Facilities in the Delta Source Region Downstream of Major Dams

Facility Type	Proximity to Delta/Yolo Bypass		Total
	Delta/ Yolo Bypass	Upstream of Delta/ Yolo Bypass	
Aggregate & Lake Dewatering	37	26	**63**
Drinking Water Treatment		6.4	**6.4**
Groundwater Remediation	0.36	48.3	**49**
Manufacturing		18	**18**
Municipal WWTP	2,348	1,085	**3,435**
Paper Mill / Saw Mills		16	**16**
Power Generation	0.27		**0.27**
Power/Domestic WWTP		0.10	**0.10**
Publishing		0.62	**0.62**
Total	**2,386**	**1,200**	**3,586**
% of Total Loads			
Aggregate & Lake Dewatering	1.0%	0.7%	**1.8%**
Drinking Water Treatment		0.2%	**0.18%**
Groundwater Remediation	0.01%	1.35%	**1.4%**
Manufacturing		0.5%	**0.5%**
Municipal WWTP	65.5%	30.3%	**95.7%**
Paper Mill / Saw Mills		0.45%	**0.45%**
Power Generation	0.008%		**0.008%**
Power/Domestic WWTP		0.003%	**0.003%**
Publishing		0.02%	**0.02%**
Total	**67%**	**33%**	**100%**

Table 36: Sum of Annual Methylmercury Loads (g/yr) Discharged by Facilities within Each Discharger Category for NPDES Facilities in the Delta Source Region Downstream of Major Dams

Facility Type	Proximity to Delta/Yolo Bypass		Total
	Delta/ Yolo Bypass	Upstream of Delta/ Yolo Bypass	
Aggregate & Lake Dewatering	0.38	0.055	**0.44**
Drinking Water Treatment		0.040	**0.040**
Food Processing		0.040	**0.040**
Groundwater Remediation	0.011	0.23	**0.24**
Laboratory		0.0047	**0.0047**
Manufacturing		0.14	**0.14**
Mines		0.0048	**0.0048**
Municipal WWTP	204.3	23.4	**228**
Paper Mill / Saw Mills		0.22	**0.22**
Power Generation	0.0019		**0.0019**
Power/Domestic WWTP		0.0050	**0.0050**
Publishing		0.0041	**0.0041**
Total	**204.7**	**23.7**	**229**
% of Total Loads			
Aggregate & Lake Dewatering	0.2%	0.02%	**0.2%**
Drinking Water Treatment		0.02%	**0.02%**
Food Processing		0.02%	**0.02%**
Groundwater Remediation	0.005%	0.1%	**0.1%**
Laboratory		0.002%	**0.002%**
Manufacturing		0.06%	**0.06%**
Mines		0.002%	**0.002%**
Municipal WWTP	89.3%	10.2%	**99.5%**
Paper Mill / Saw Mills		0.1%	**0.1%**
Power Generation	0.001%		**0.001%**
Power/Domestic WWTP		0.002%	**0.002%**
Publishing		0.002%	**0.002%**
Total	**89%**	**11%**	**100%**

Table 37: Comparison of Annual Methylmercury Loads (g/yr) Discharged by NPDES Facilities to The Sum of All Point and Nonpoint Source Methylmercury Loading to Each Delta Subarea Identified in The February 2010 Delta TMDL Staff Report (Wood *et al*., 2010b, Table 8.4)

Delta Subarea	**Proximity to Delta**		**Total NPDES Facility Load**	**Sum of MeHg Point and Nonpoint Source MeHg Loads to Each Subarea** [Delta TMDL Report Table 8.4]	**Total NPDES Facility Load as % of Sum of All Point and Nonpoint MeHg Loads**
	Delta/ Yolo Bypass	Upstream of Delta/ Yolo Bypass			
Central	1.3	*[none]*	1.3	668	0.2%
Marsh Creek	0.086	*[none]*	0.086	6.14	1.4%
Mokelumne	*[none]*	0.55	0.55	146	0.4%
Sacramento	163	13	176	2,475	7.1%
San Joaquin	39.6	8.6	48	528	9.1%
West	0.0019	none	0.0019	330	0.001%
Yolo Bypass	1.0	1.7	2.7	1,068	0.3%
TOTAL	**205**	**24**	**229**	**5,221**	**4.4%**

[(a)] Because calculations were completed prior to rounding, some columns may not add to totals shown in Table 36 of this report or Table 6.2 in the TMDL Report.

FIGURES

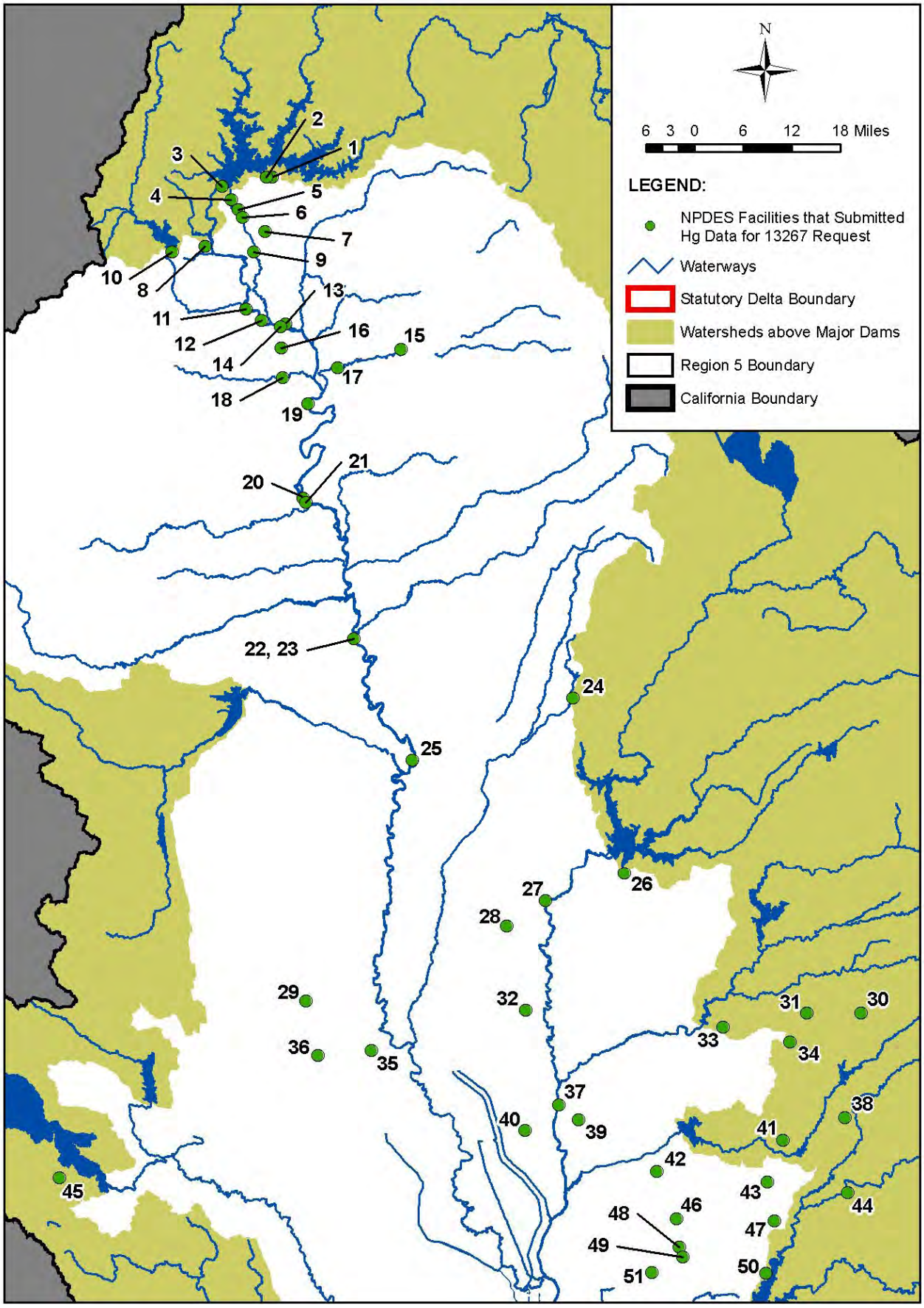

Figure 1: Location of NPDES Facilities (North Panel) [Table 16 defines facility codes]

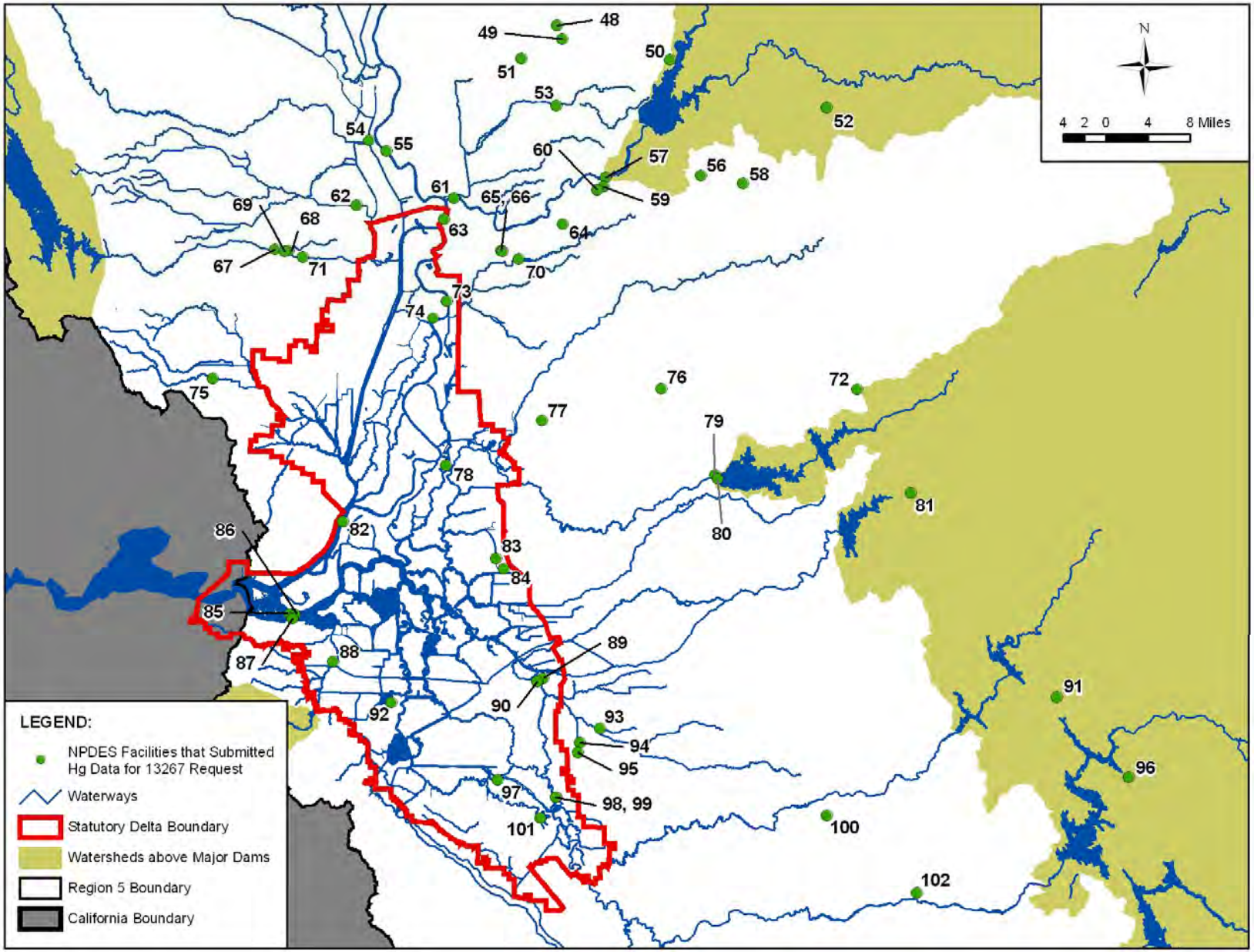

Figure 2: Location of NPDES Facilities (Central Panel) [Table 16 defines facility codes]

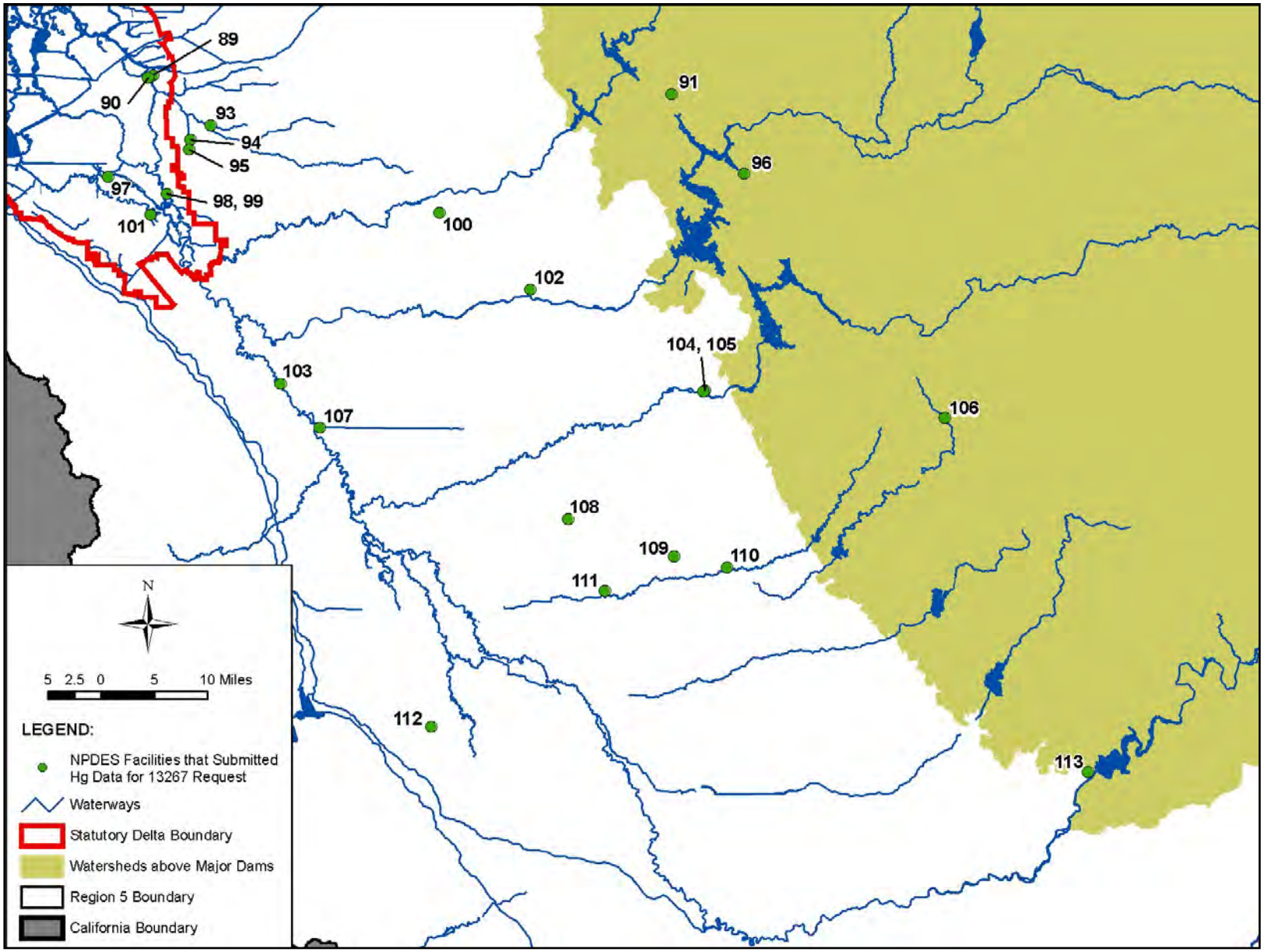

Figure 3: Location of NPDES Facilities (South Panel) [Table 16 defines facility codes]

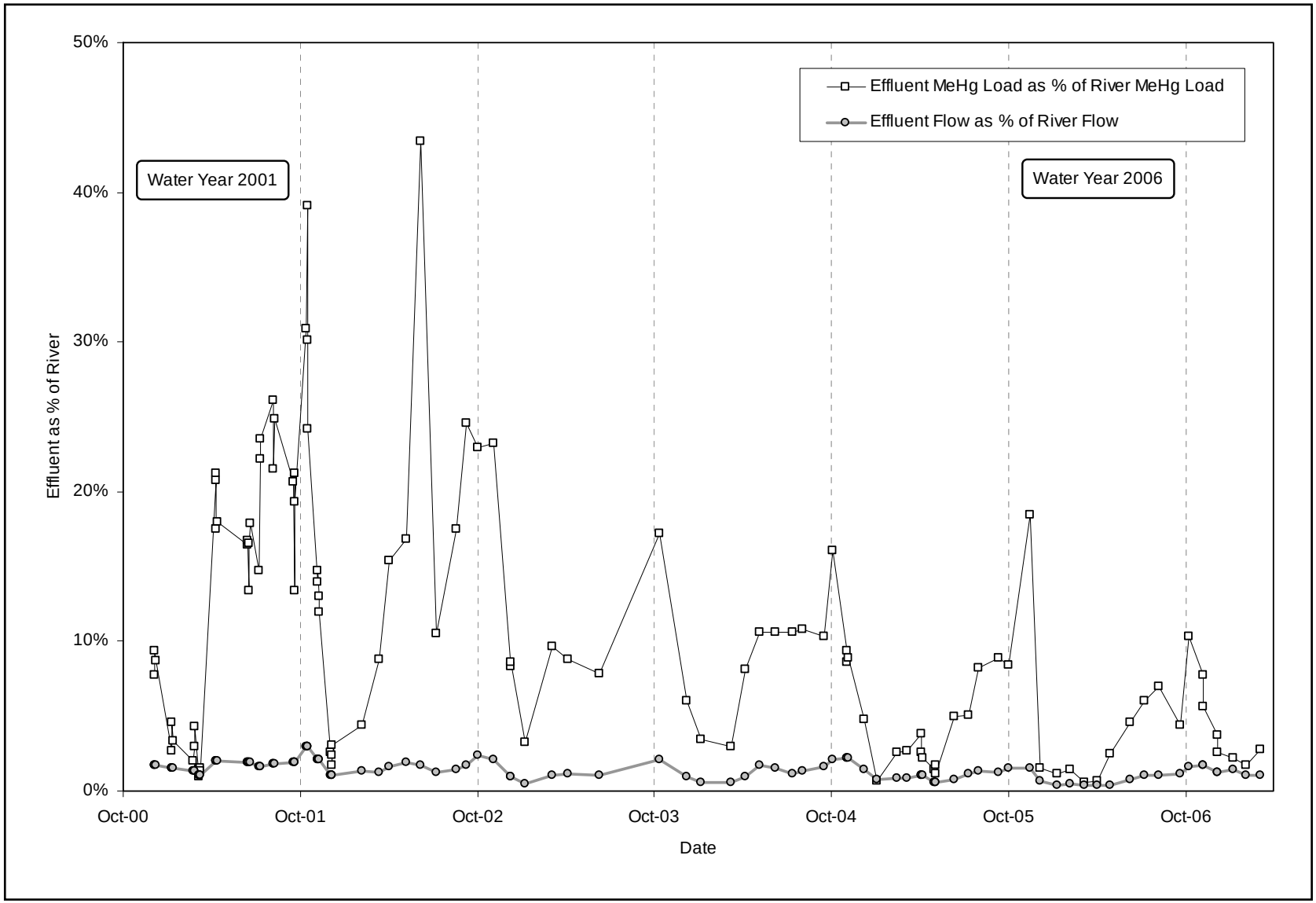

Figure 4: SRCSD Sacramento River WWTP Effluent Methylmercury Load and Flow as a Percent of Sacramento River Methylmercury Load and Flow for Water Years (WY) 2001-2007

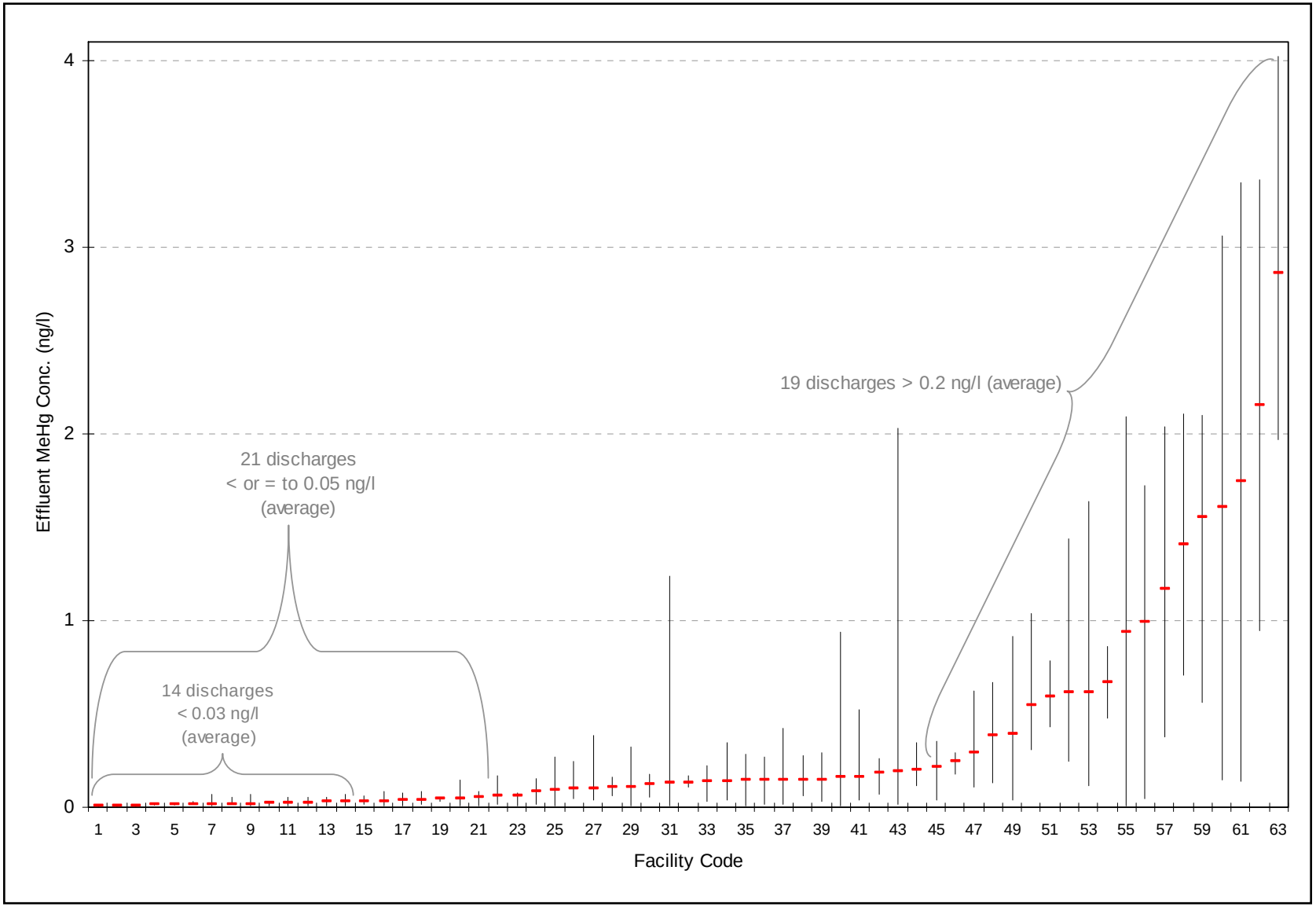

Figure 5: Average and Range of Effluent Methylmercury Concentrations for Each of the Municipal WWTP Discharges

Facility Codes Used in Figures 5 and 10 [(a)]

Facility Code	NPDES No.	Facility
1	CA0082660	Brentwood WWTP
2	CA0078093	Deuel Vocational Institute WWTP
3	CA0084697	United Auburn Indian Community Casino WWTP
4	CA0078671	El Dorado Hills WWTP (Discharge 2)
5	CA0082589	Redding Stillwater WWTP
6	CA0078662	Deer Creek WWTP
7	CA0084573	Roseville Pleasant Grove WWTP
8	CA0078671	El Dorado Hills WWTP (Discharge 1)
9	CA0084476	Lincoln WWTP
10	CA0079511	Shasta Lake WWTP
11	CA0079502	Roseville Dry Creek WWTP
12	CA0077691	Vacaville Easterly WWTP
13	CA0078891	Red Bluff WWTP
14	CA0077712	Auburn WWTP
15	CA0077950	Woodland WWTP
16	CA0079197	Atwater WWTP
17	CA0077895	UC Davis WWTP
18	CA0079731	Redding Clear Creek WWTP
19	CA0004995	Corning Industries/ Domestic WWTP
20	CA0079901	Nevada City WWTP
21	CA0079171	West Sacramento WWTP
22	CA0078956	Placerville Hangtown Creek WWTP
23	CA0078948	Turlock WWTP
24	CA0082848	San Joaquin Co DPW - Flag City WWTP
25	CA0077704	Anderson WWTP
26	CA0081507	Cottonwood WWTP
27	CA0079367	Placer Co. SMD #3 WWTP
28	CA0079391	Jackson WWTP
29	CA0077828	Nevada Co SD #1 Lake Wildwood WWTP
30	CA0079081	Chico Regional WWTP
31	CA0079243	Lodi White Slough WWTP
32	CA0079103	Modesto WWTP
33	CA0081434	Galt WWTP
34	CA0079316	Placer Co. SMD #1 WWTP
35	CA0083241	Nevada Co SD #1 Cascade Shores WWTP
36	CA0077836	Olivehurst PUD WWTP
37	CA0079154	Tracy WWTP
38	CA0079235	Oroville WWTP
39	CA0083682	Canada Cove LP French Camp Golf & RV Park WWTP
40	CA0079898	Grass Valley WWTP

Facility Codes Used in Figures 5 and 10 [(a)]

Facility Code	NPDES No.	Facility
41	CA0079588	Rio Vista Main WWTP
42	CA0084727	Tuolumne UD Sonora RWTP/ Jamestown SDWTP
43	CA0078590	Discovery Bay WWTP
44	CA0079529	Colfax WWTP
45	CA0081558	Manteca WWTP
46	CA0079464	San Andreas SD WWTP
47	CA0079260	Yuba City WWTP
48	CA0079219	Merced WWTP
49	CA0079430	Mariposa PUD WWTP
50	CA0079049	Davis WWTP (Discharge 1)
51	CA0079022	Live Oak WWTP
52	CA0079049	Davis WWTP (Discharge 2)
53	CA0077682	SRCSD Sacramento River WWTP
54	CA0079341	Placer Co. SA #28 Zone #6 WWTP
55	CA0079138	Stockton WWTP
56	CA0079987	Maxwell PUD WWTP
57	CA0078950	Planada Comm. Service Dist. WWTP
58	CA0081612	Nevada Co SD #2 Lake of the Pines WWTP
59	CA0077933	Williams WWTP
60	CA0078930	Biggs WWTP
61	CA0077852	Rio Alto WD- Lake CA WWTP
62	CA0078794	SRCSD Walnut Grove WWTP (CSD1)
63	CA0078999	Colusa WWTP

[(a)] Facilities are sorted by lowest to highest average effluent methylmercury concentration. Some facilities have multiple discharge locations, effluent from which may undergo different treatments.

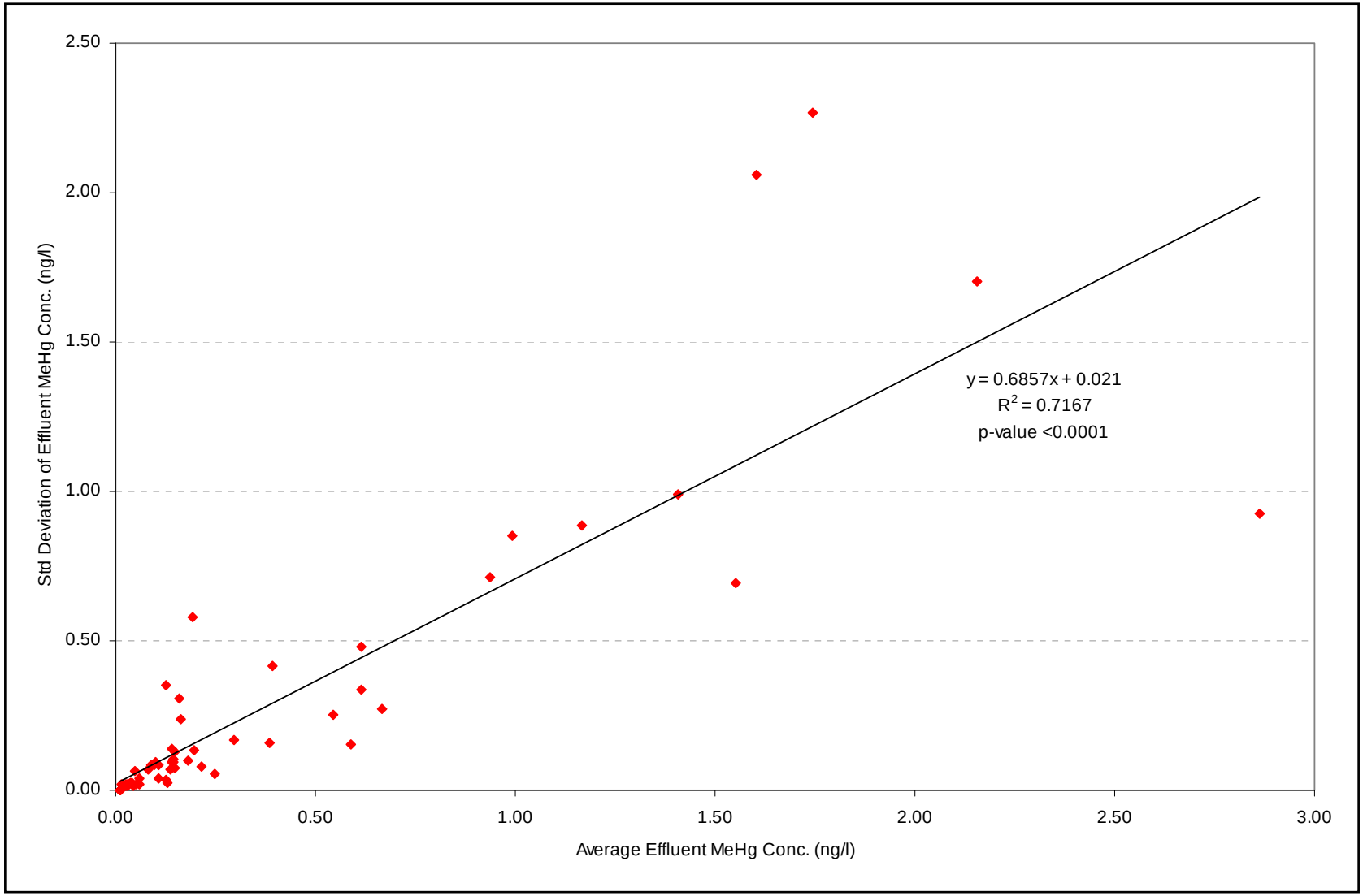

Figure 6: Average Effluent Methylmercury Concentration Versus the Corresponding Standard Deviation of Each Municipal WWTP

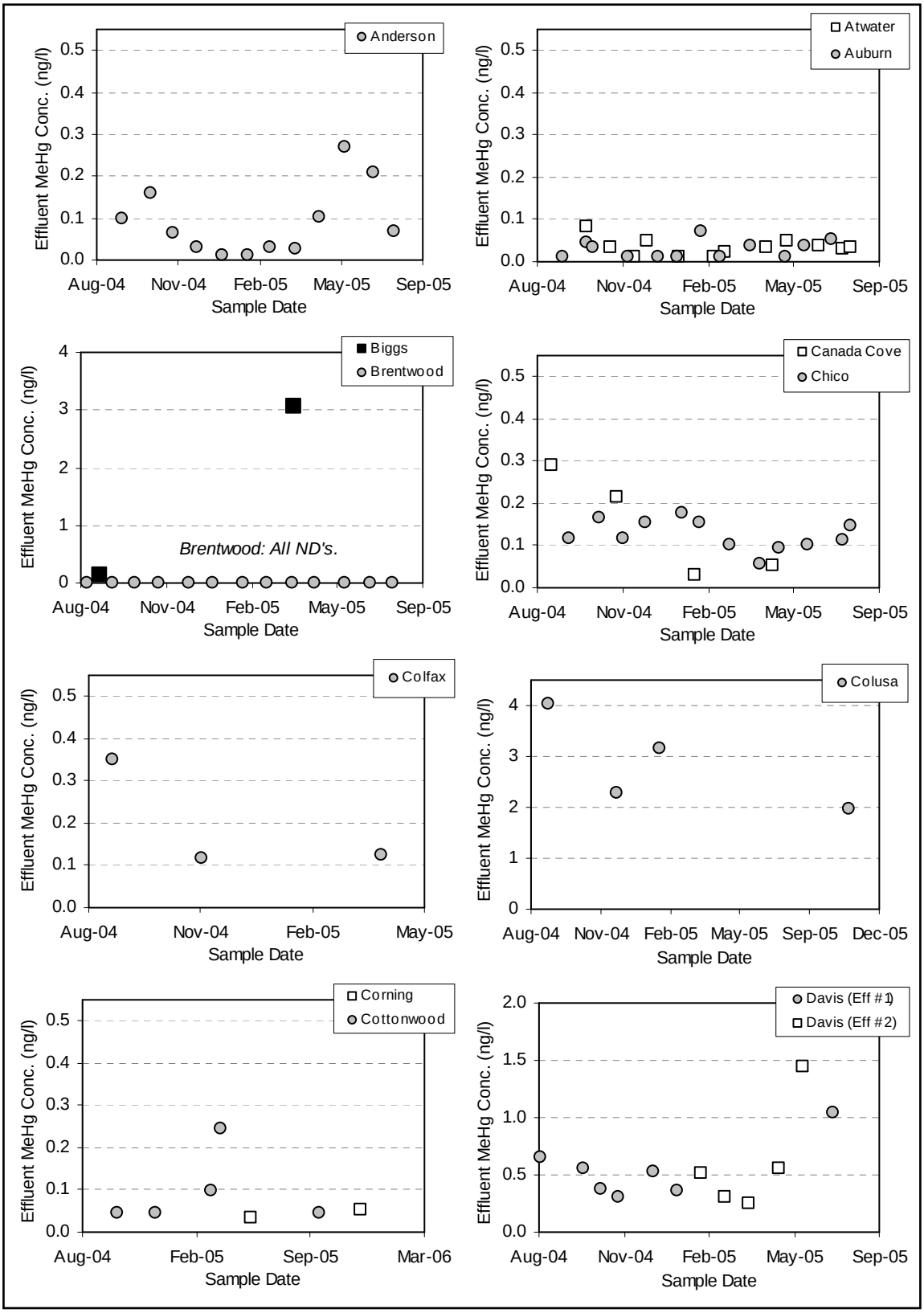

Figure 7a: Time-series Graphs of Municipal WWTP Effluent Methylmercury Concentrations

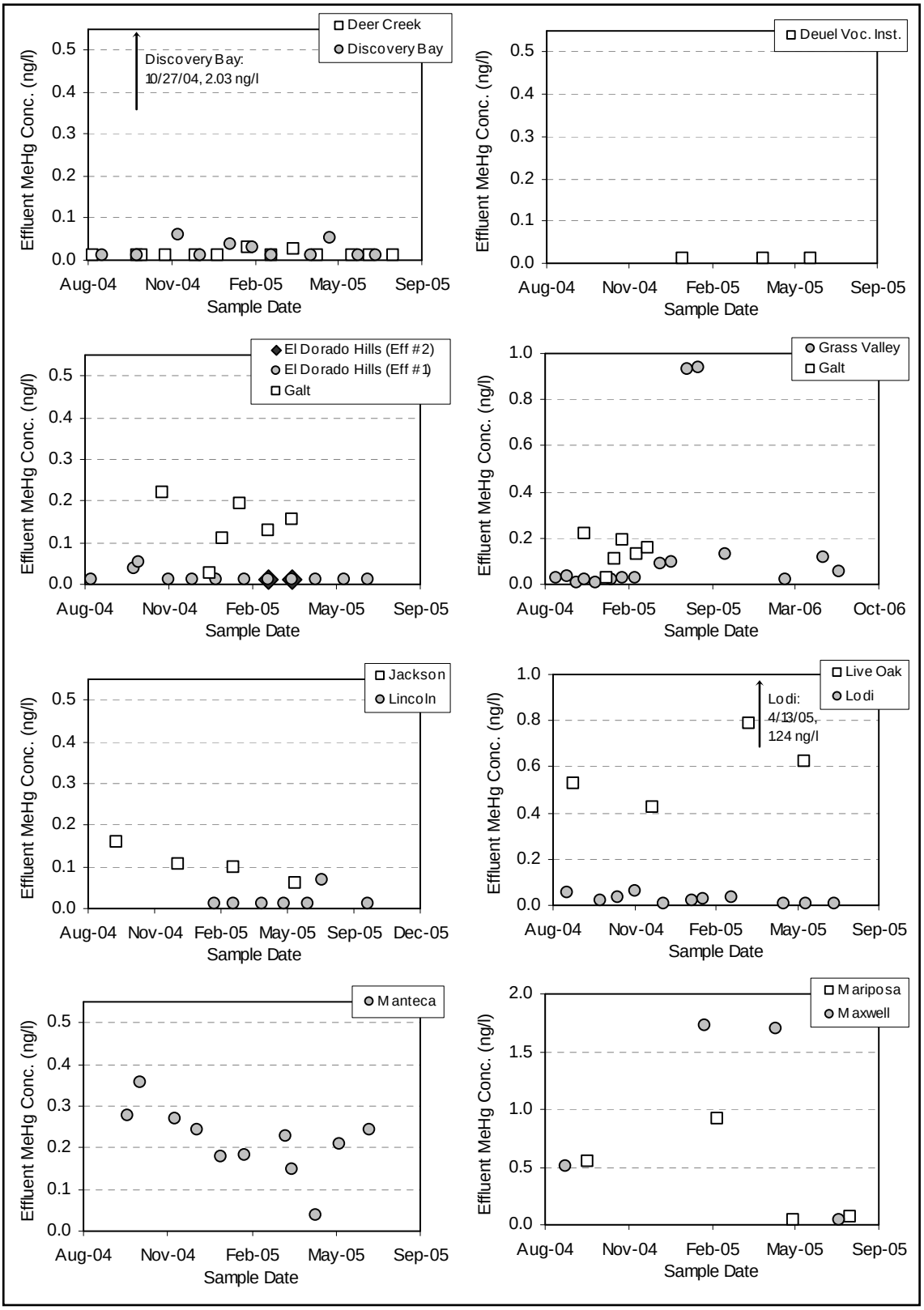

Figure 7b: Time-series Graphs of Municipal WWTP Effluent Methylmercury Concentrations

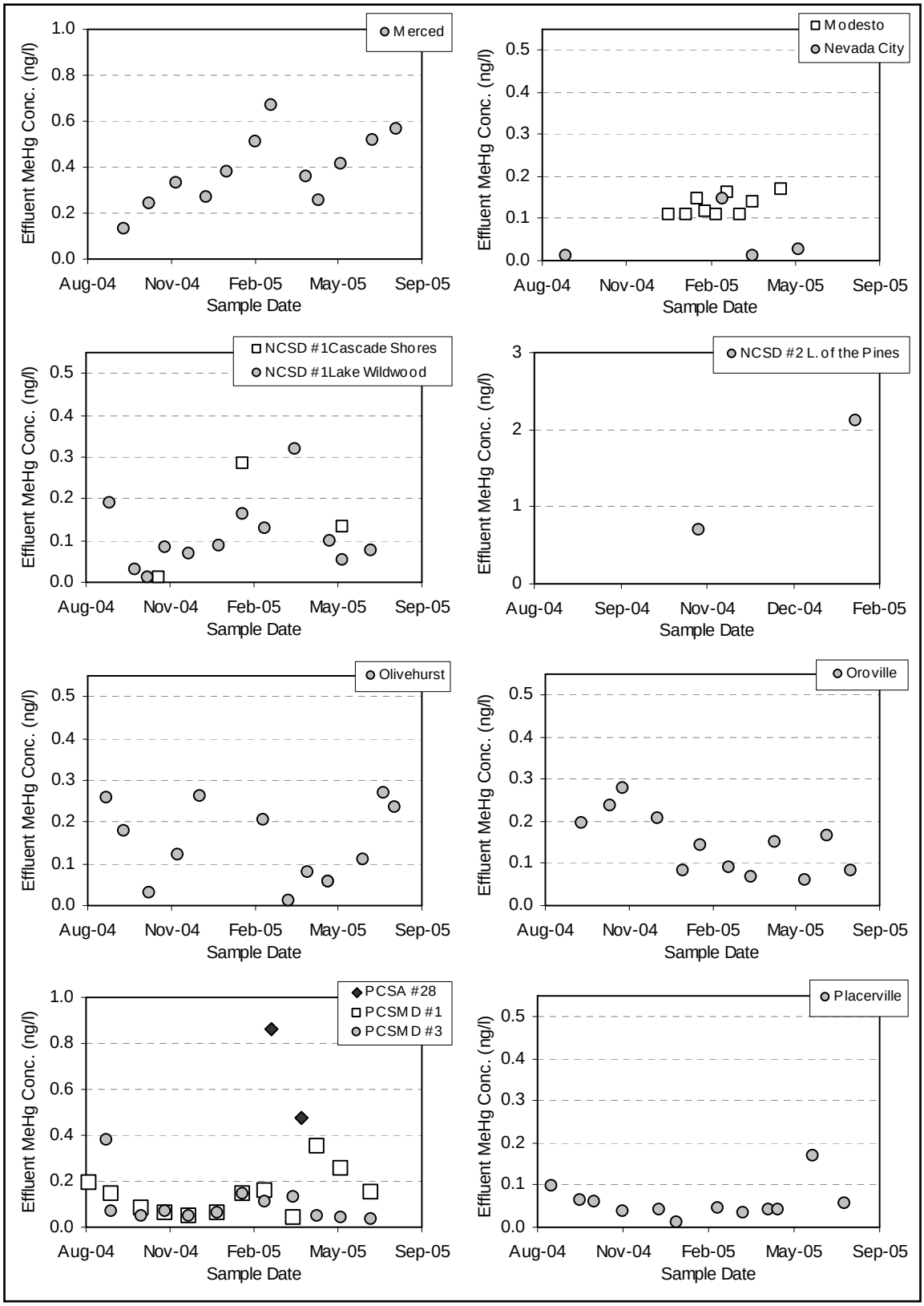

Figure 7c: Time-series Graphs of Municipal WWTP Effluent Methylmercury Concentrations

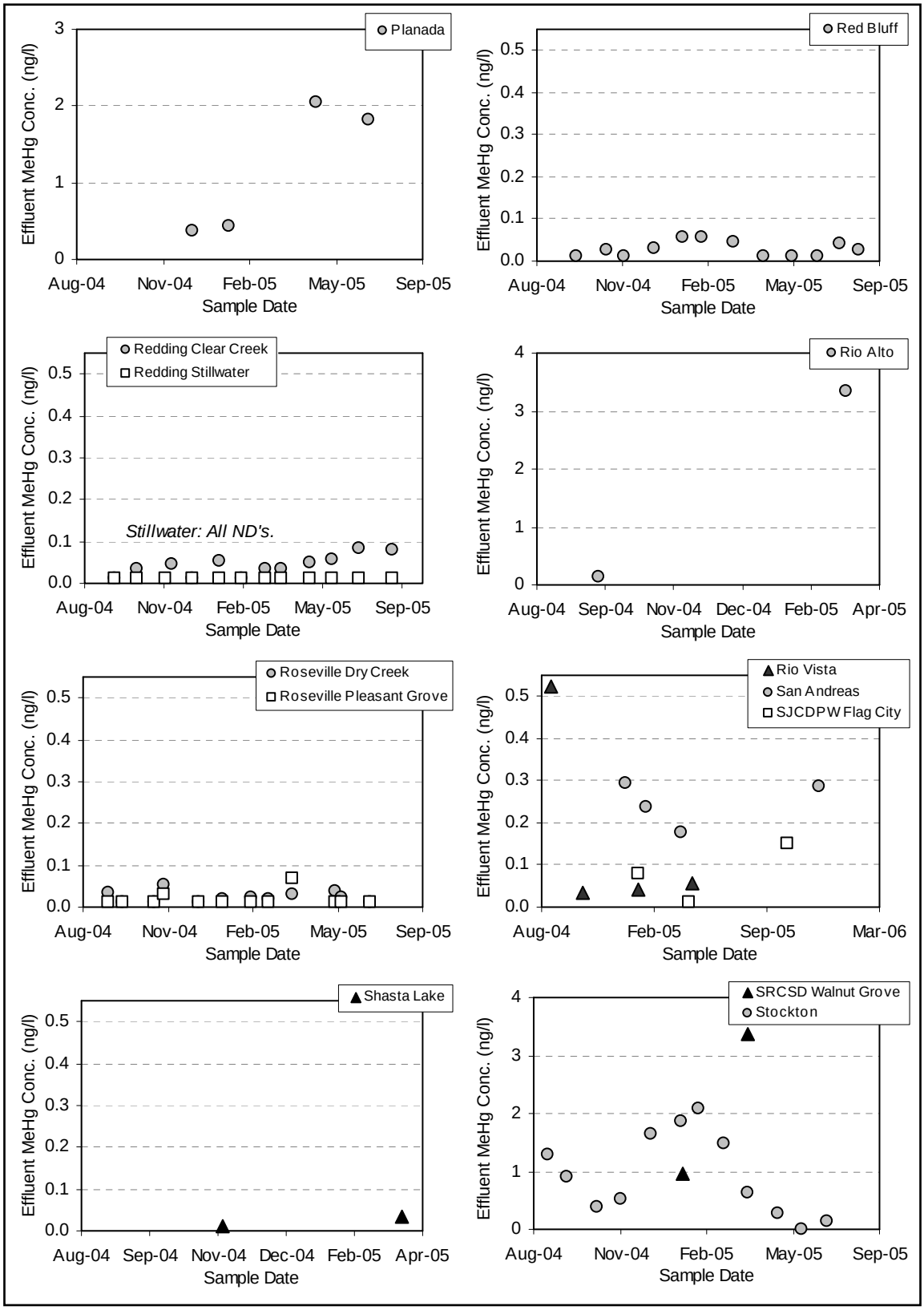

Figure 7d: Time-series Graphs of Municipal WWTP Effluent Methylmercury Concentrations

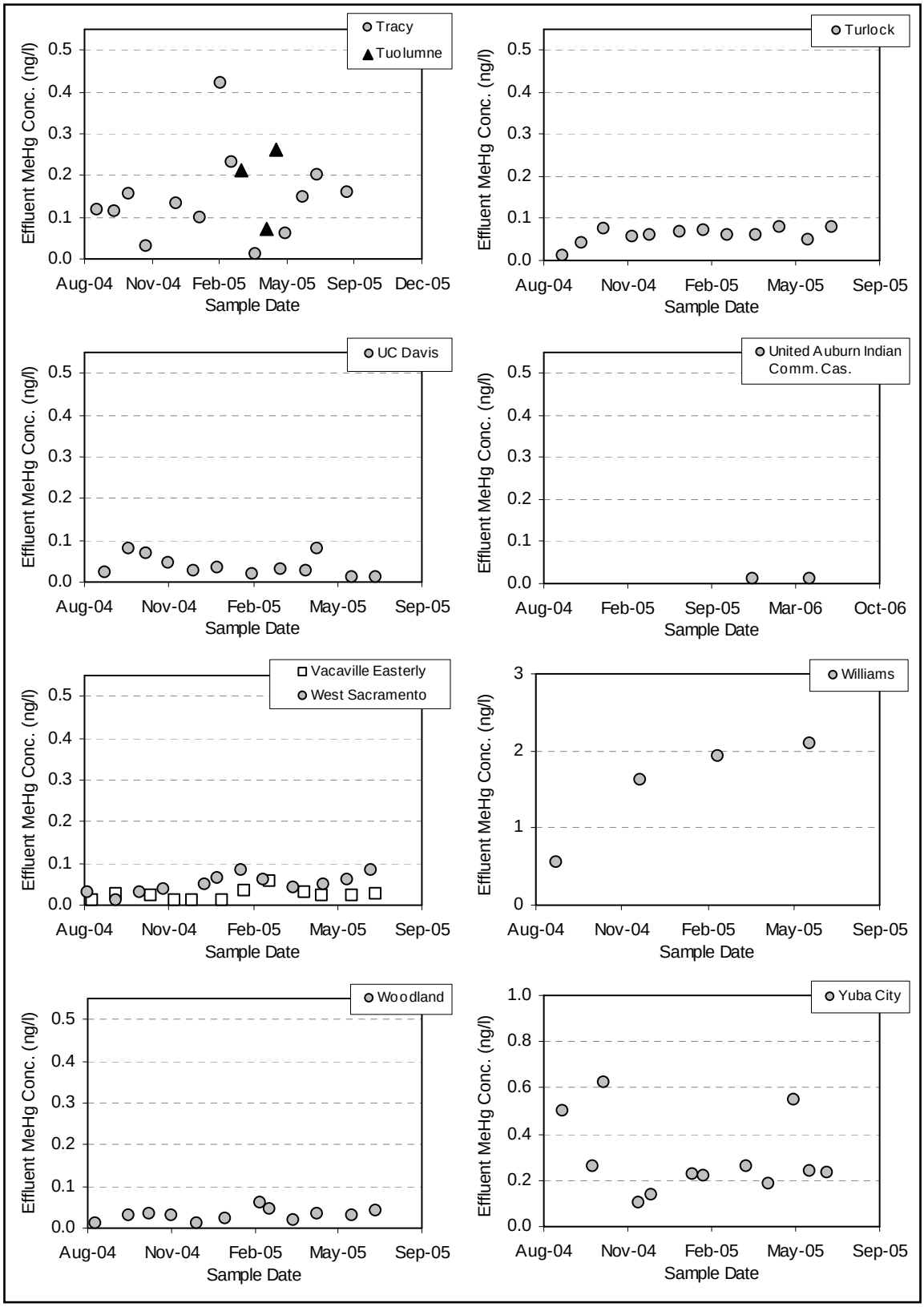

Figure 7e: Time-series Graphs of Municipal WWTP Effluent Methylmercury Concentrations

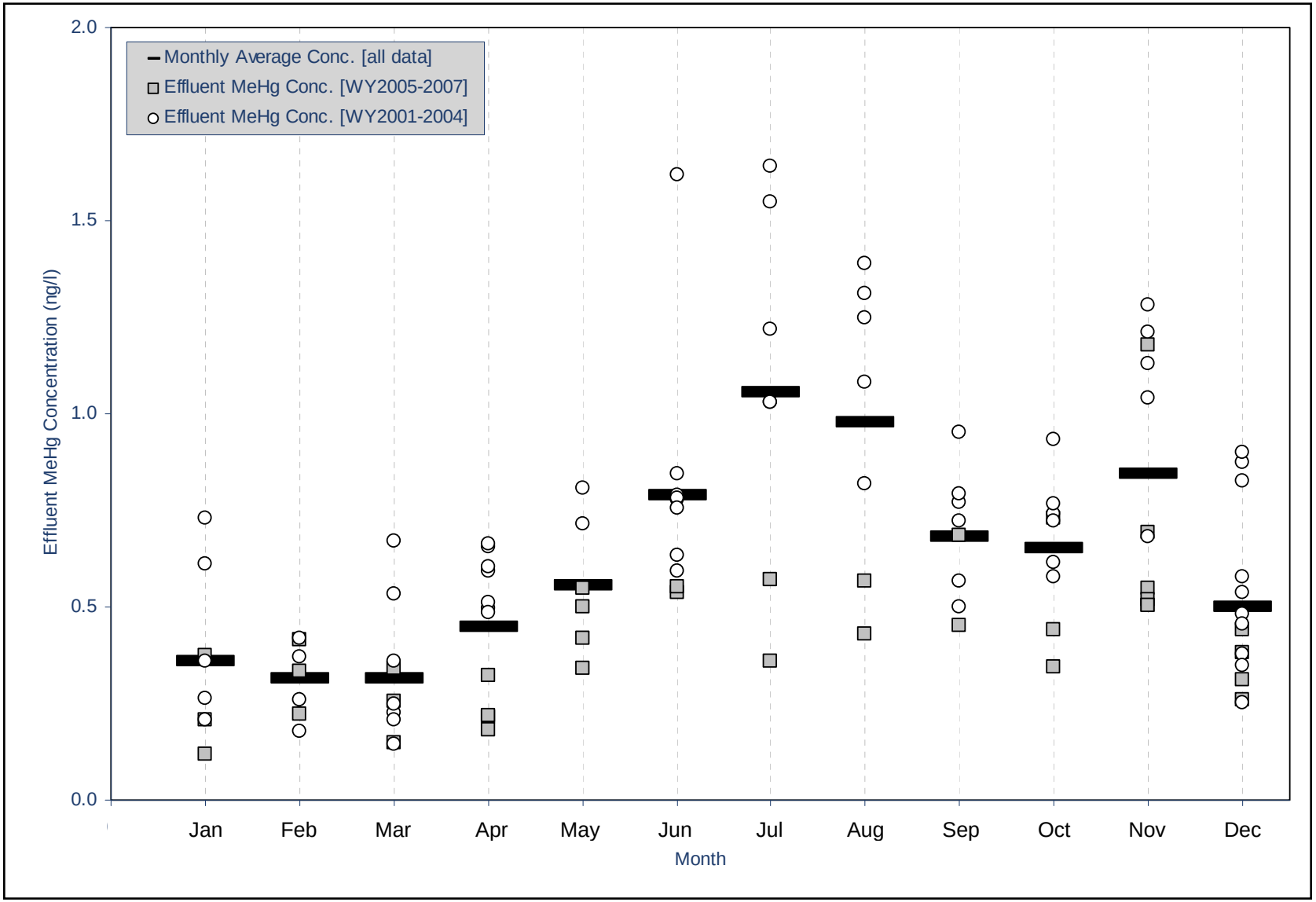

Figure 8: Monthly Effluent Methylmercury Concentrations for the SRCSD Sacramento River WWTP for WY2001-2007

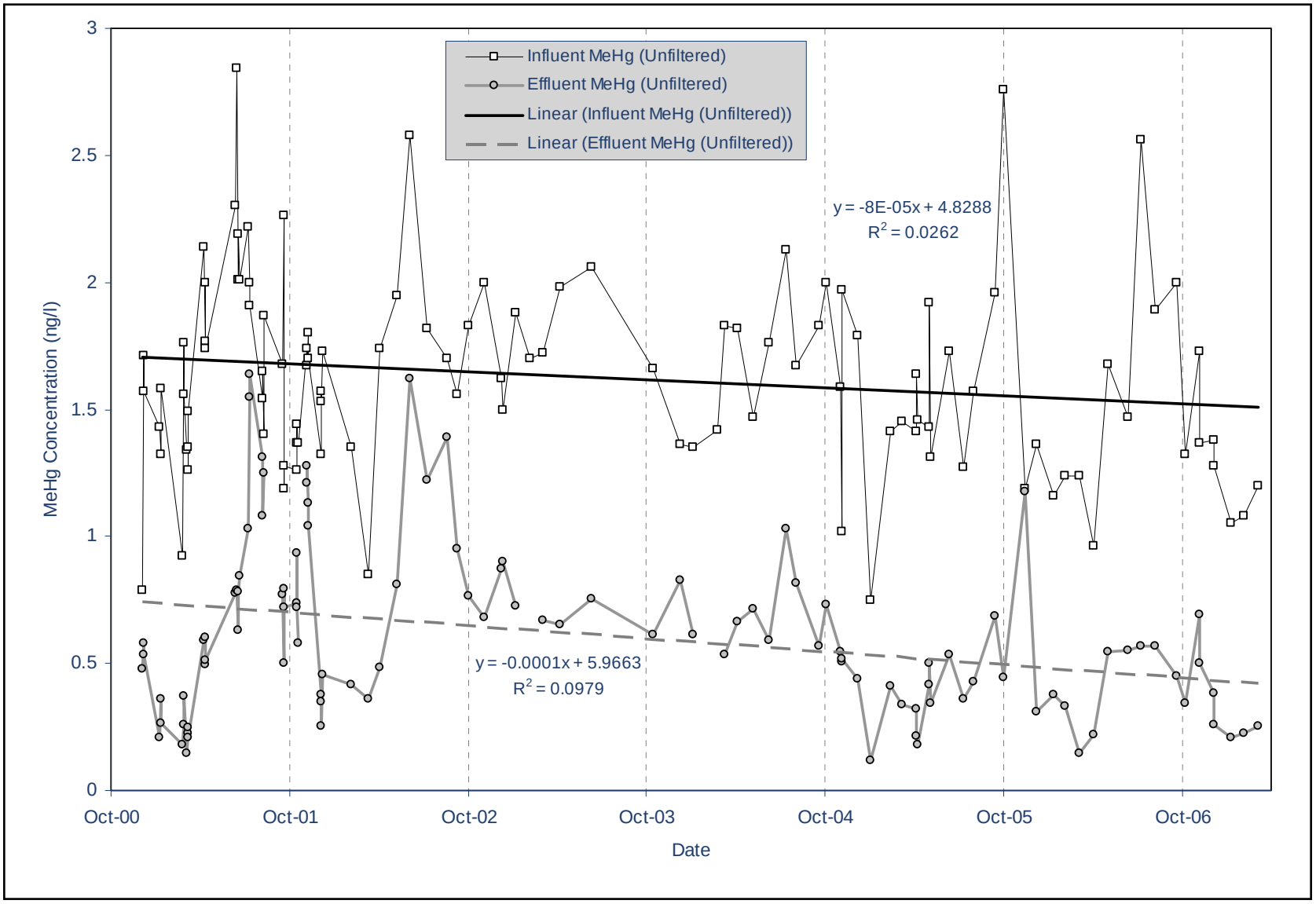

Figure 9: Time-series Graph for SRCSD Sacramento River WWTP Influent and Effluent Methylmercury Concentrations

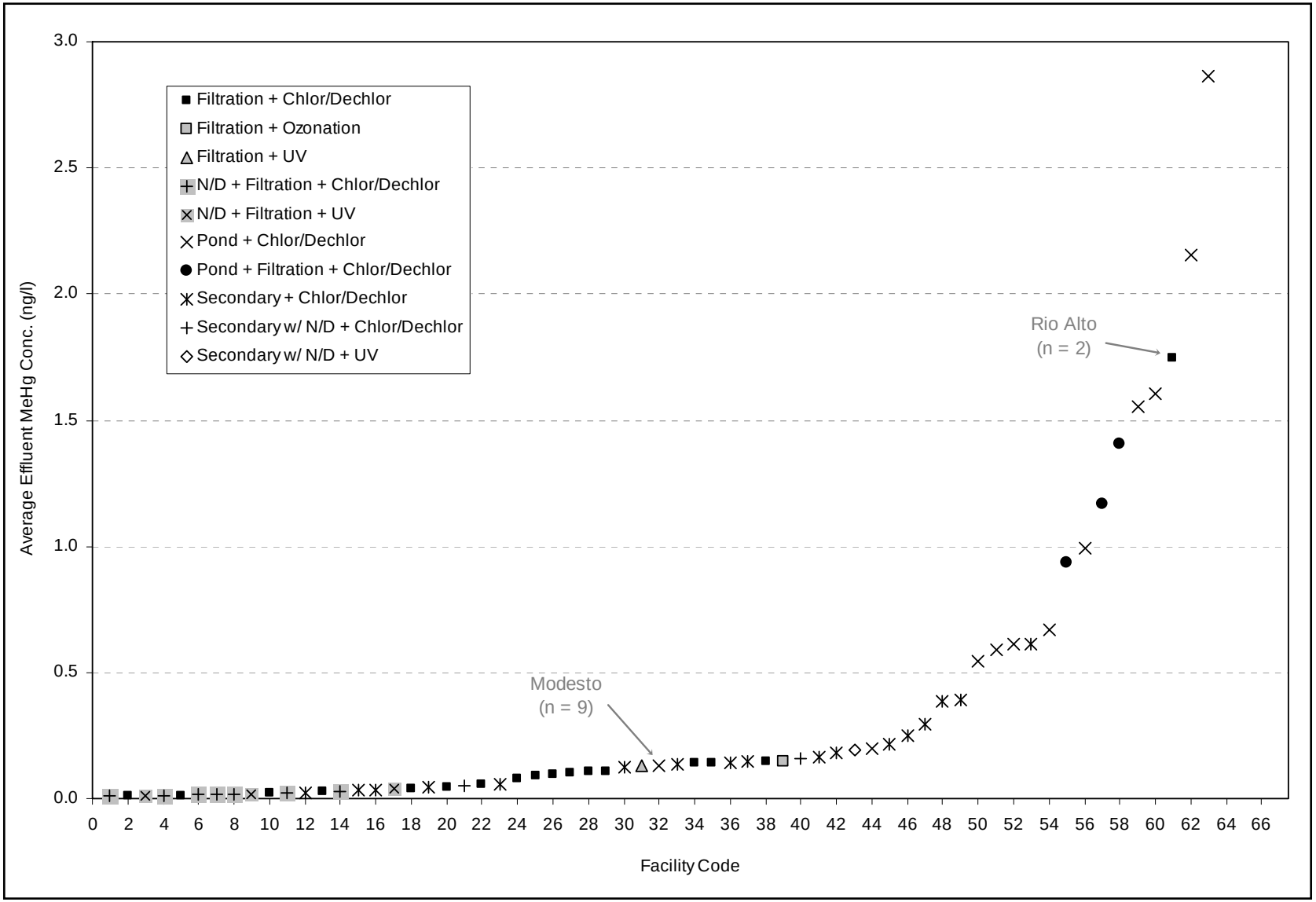

Figure 10: Average Effluent Methylmercury Concentrations for Each Municipal WWTP with the Maximum Treatment Category Defined
[WWTPs with relatively high or low effluent methylmercury concentrations compared to other WWTPs within the same maximum treatment category are labeled.]

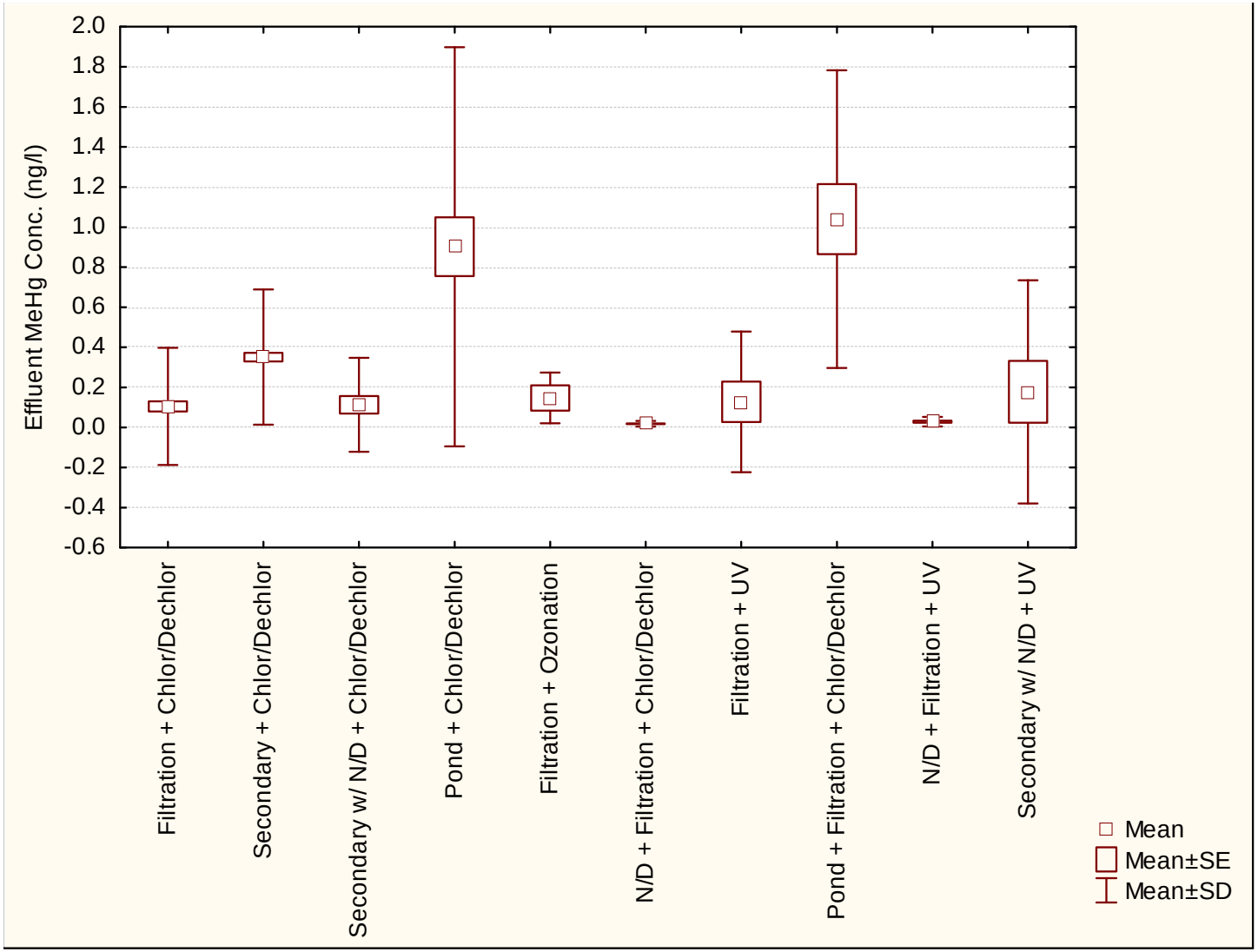

Figure 11: Box and Whisker Plot of Effluent Methylmercury Concentrations for the Municipal WWTP Maximum Treatment Categories

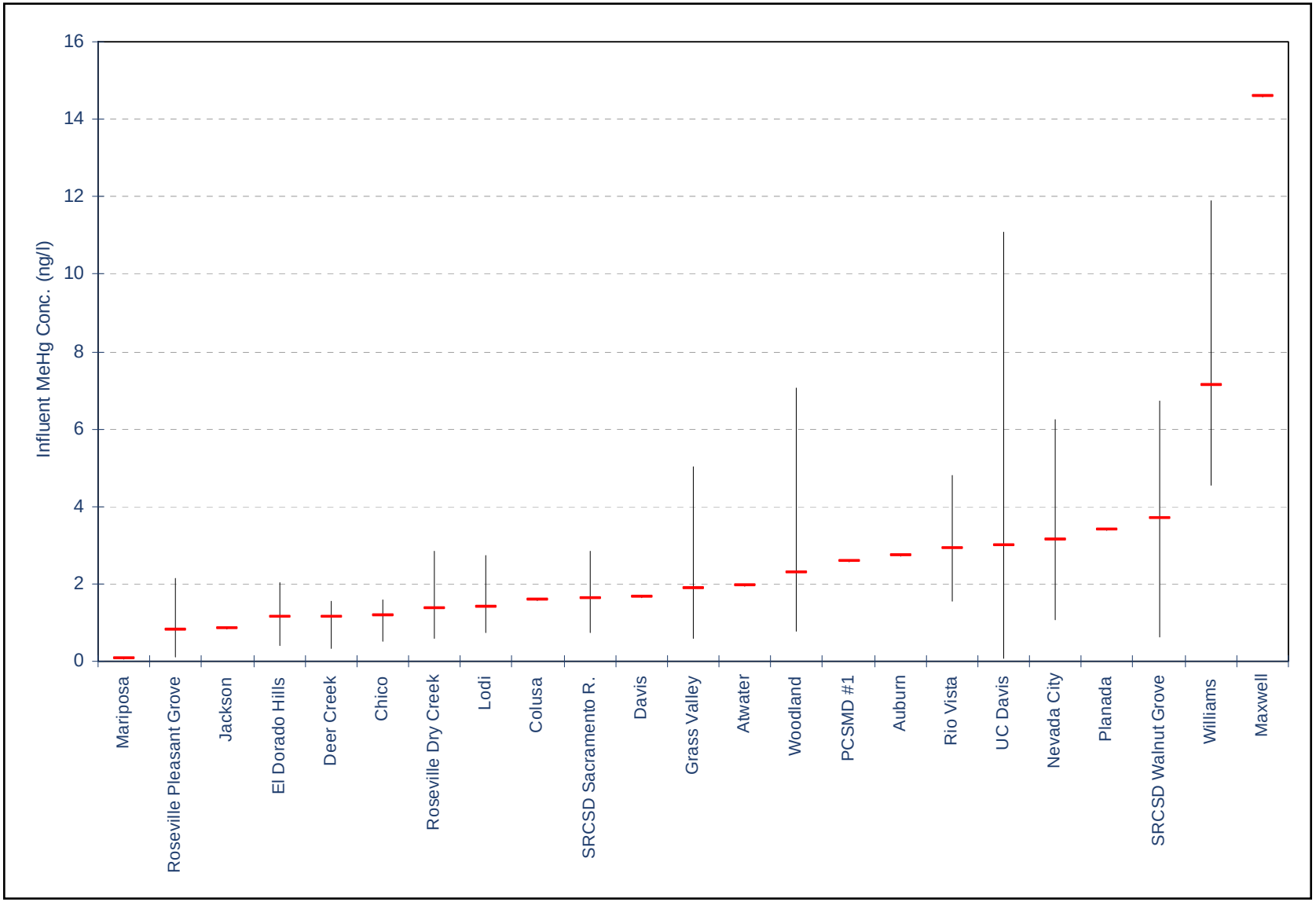

Figure 12: Average and Range of Influent Methylmercury Concentrations for Each Municipal WWTP

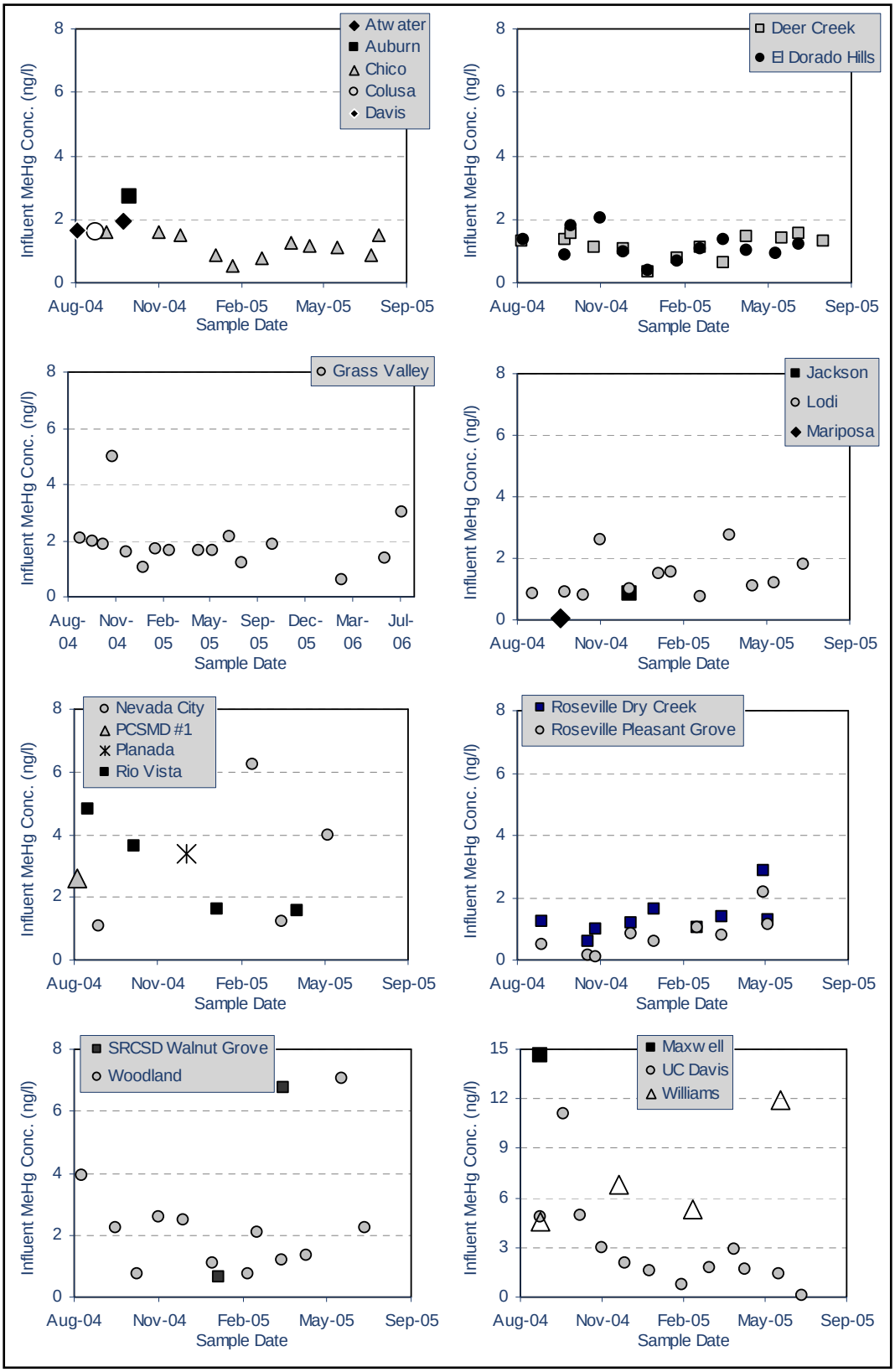

Figure 13: Time-series Graphs of Municipal WWTP Influent Methylmercury Concentrations

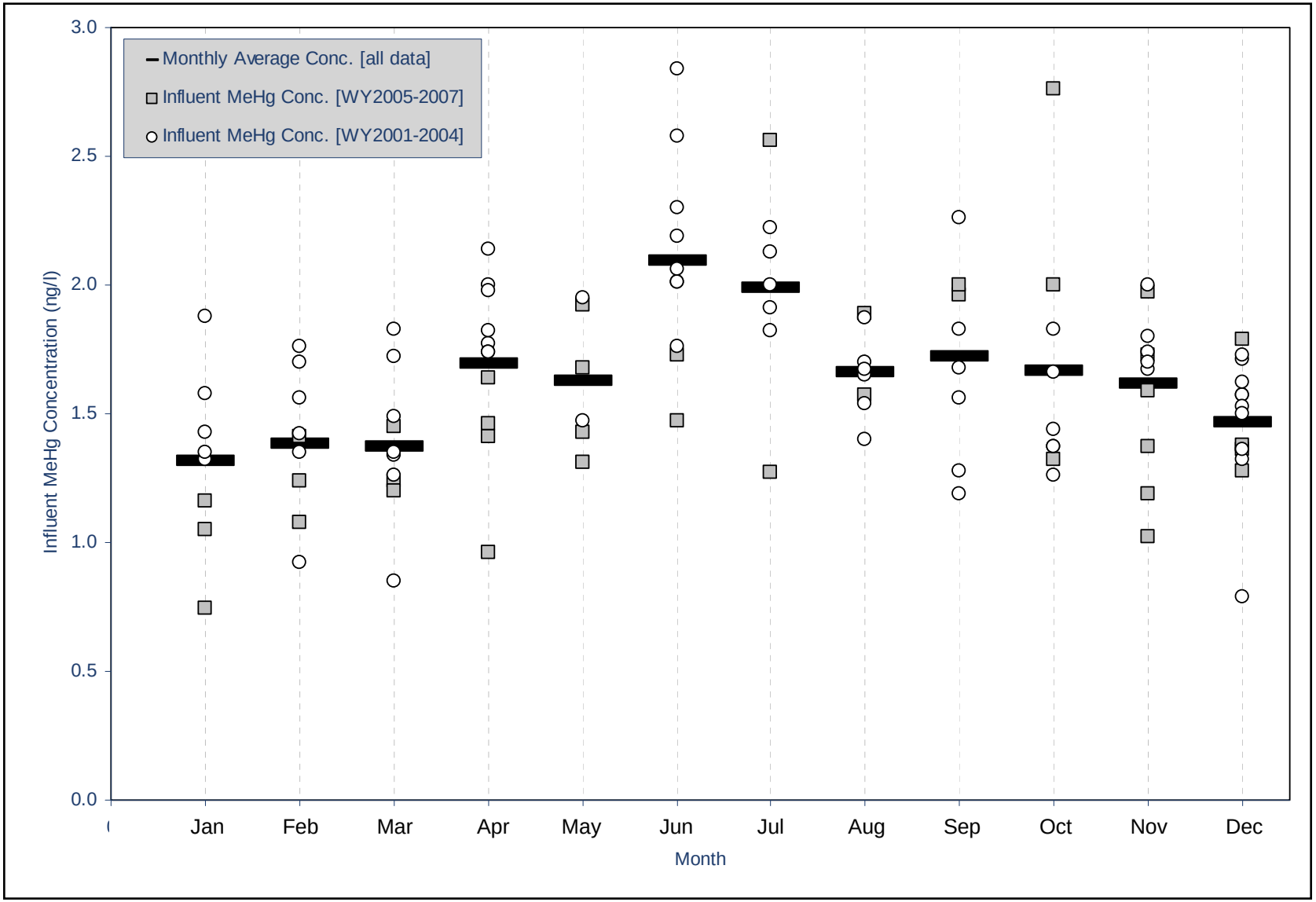

Figure 14: Monthly Influent Methylmercury Concentrations for the SRCSD Sacramento River WWTP from WY2001-2007

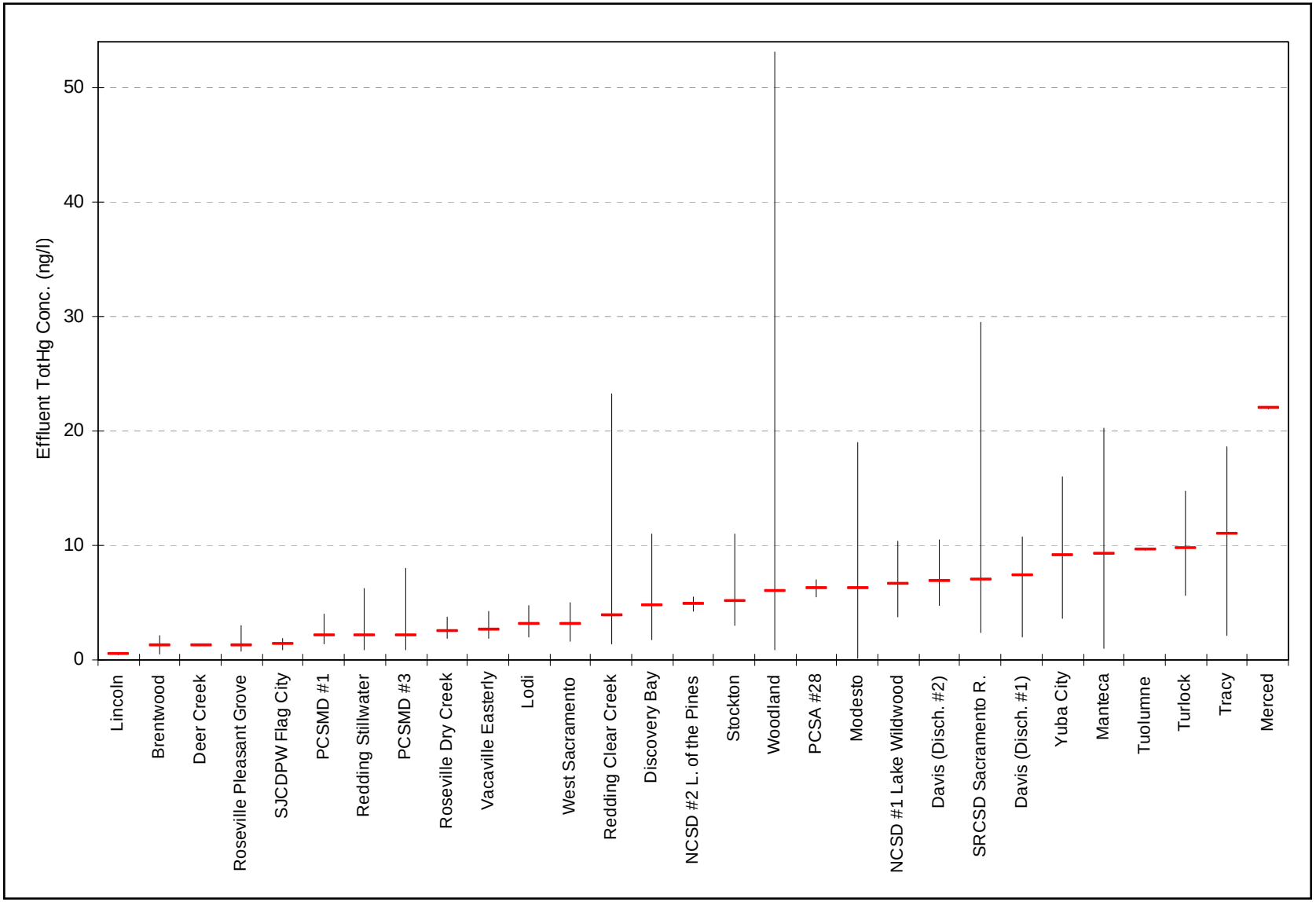

Figure 15: Average and Range of Effluent Inorganic Mercury Concentrations for Each Municipal WWTP

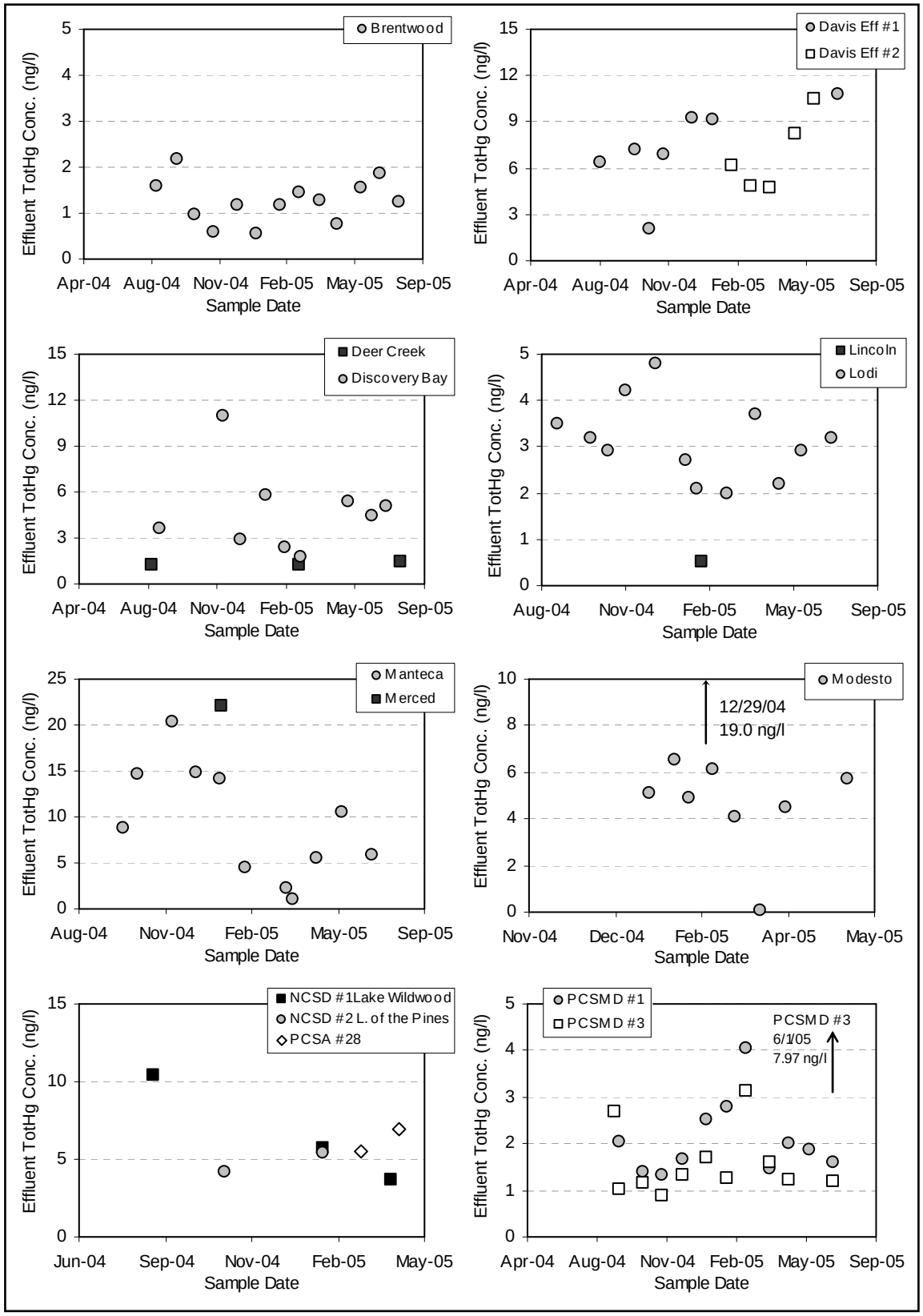

Figure 16a: Time-series Graphs of Municipal WWTP Effluent Inorganic Mercury Concentrations

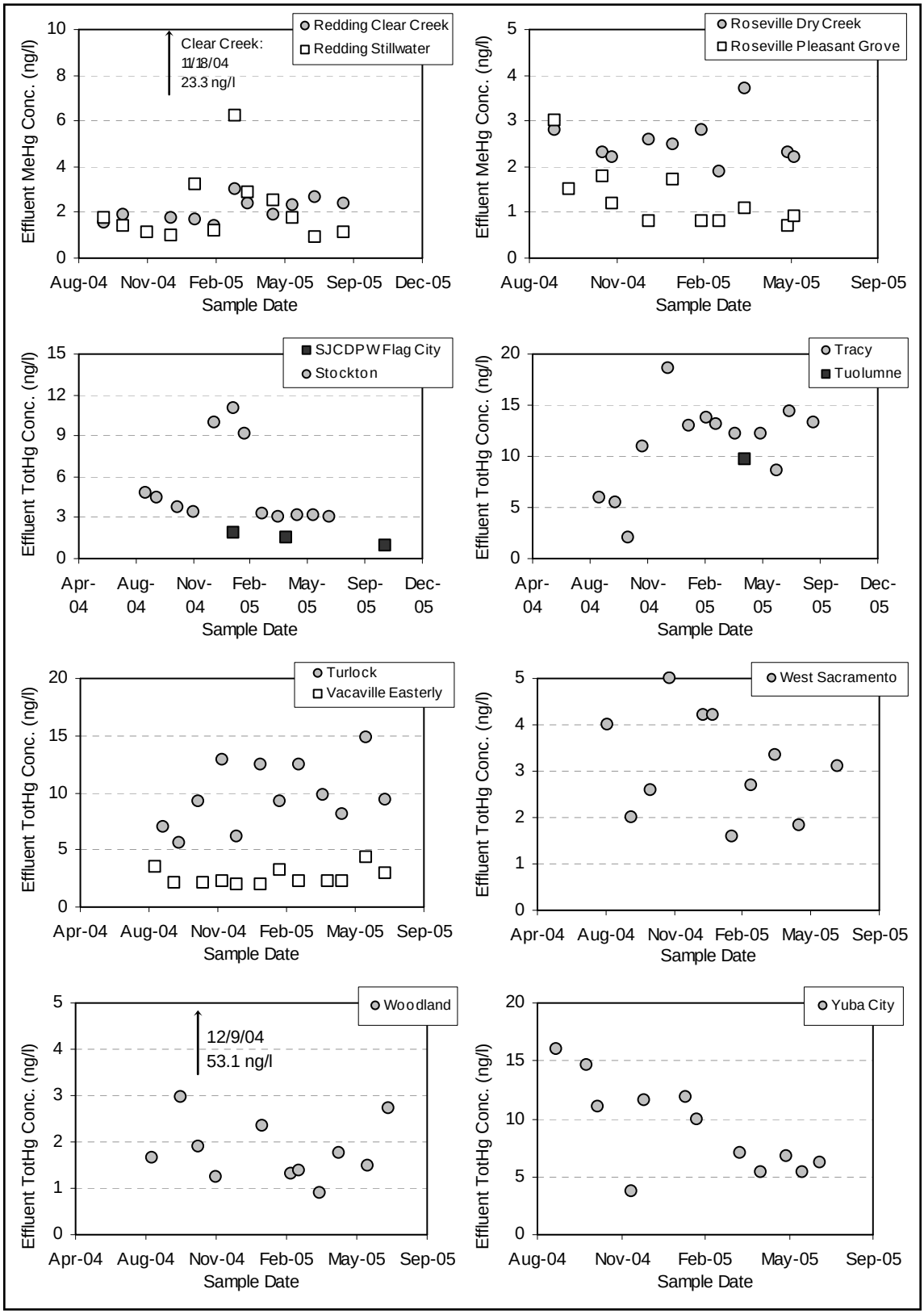

Figure 16b: Time-series Graphs of Municipal WWTP Effluent Inorganic Mercury Concentrations

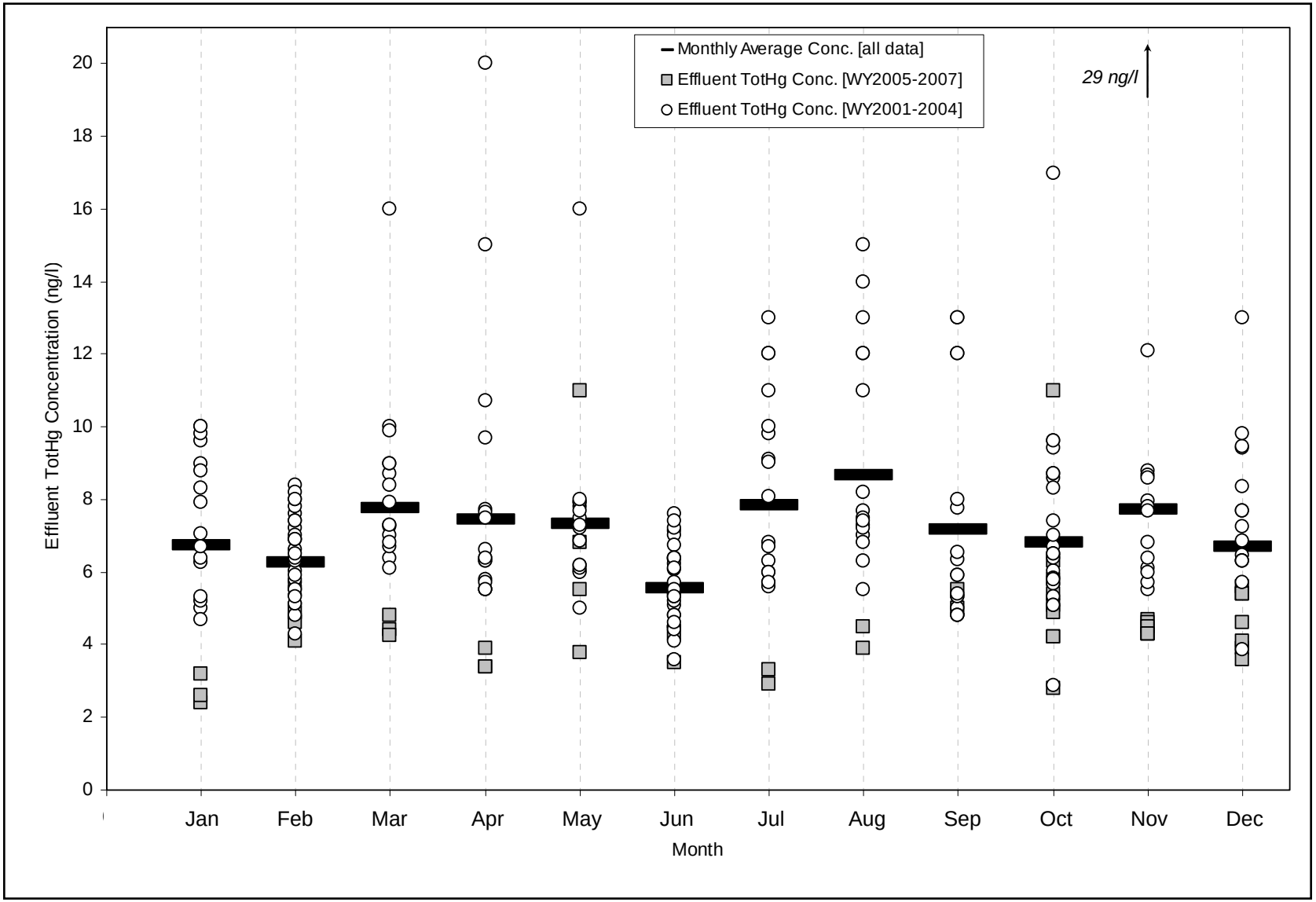

Figure 17: Monthly Effluent Inorganic Mercury Concentrations for the SRCSD Sacramento River WWTP from WY2001-2007

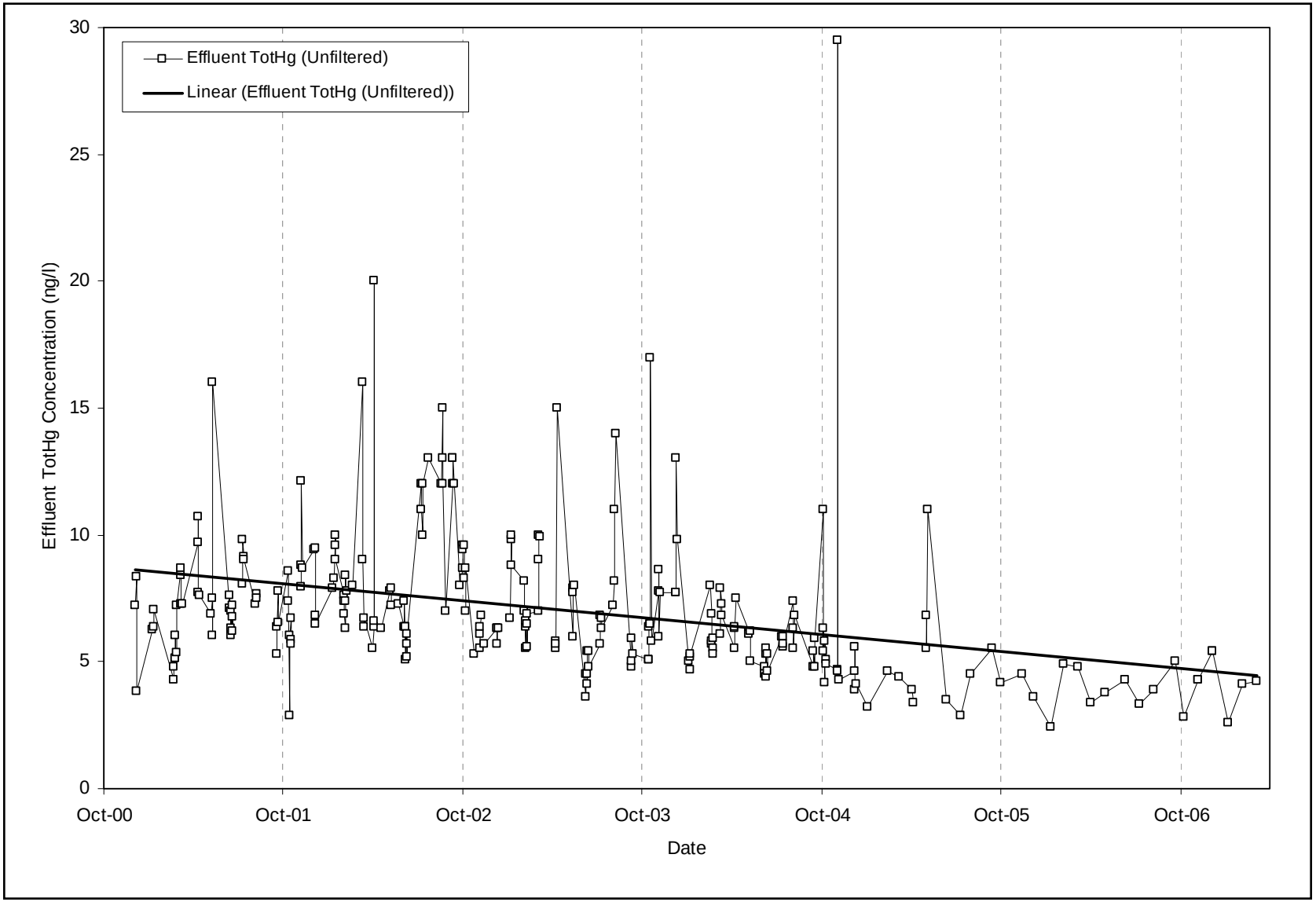

Figure 18: Time-series Graph of SRCSD Sacramento River WWTP Effluent Inorganic Mercury Concentrations

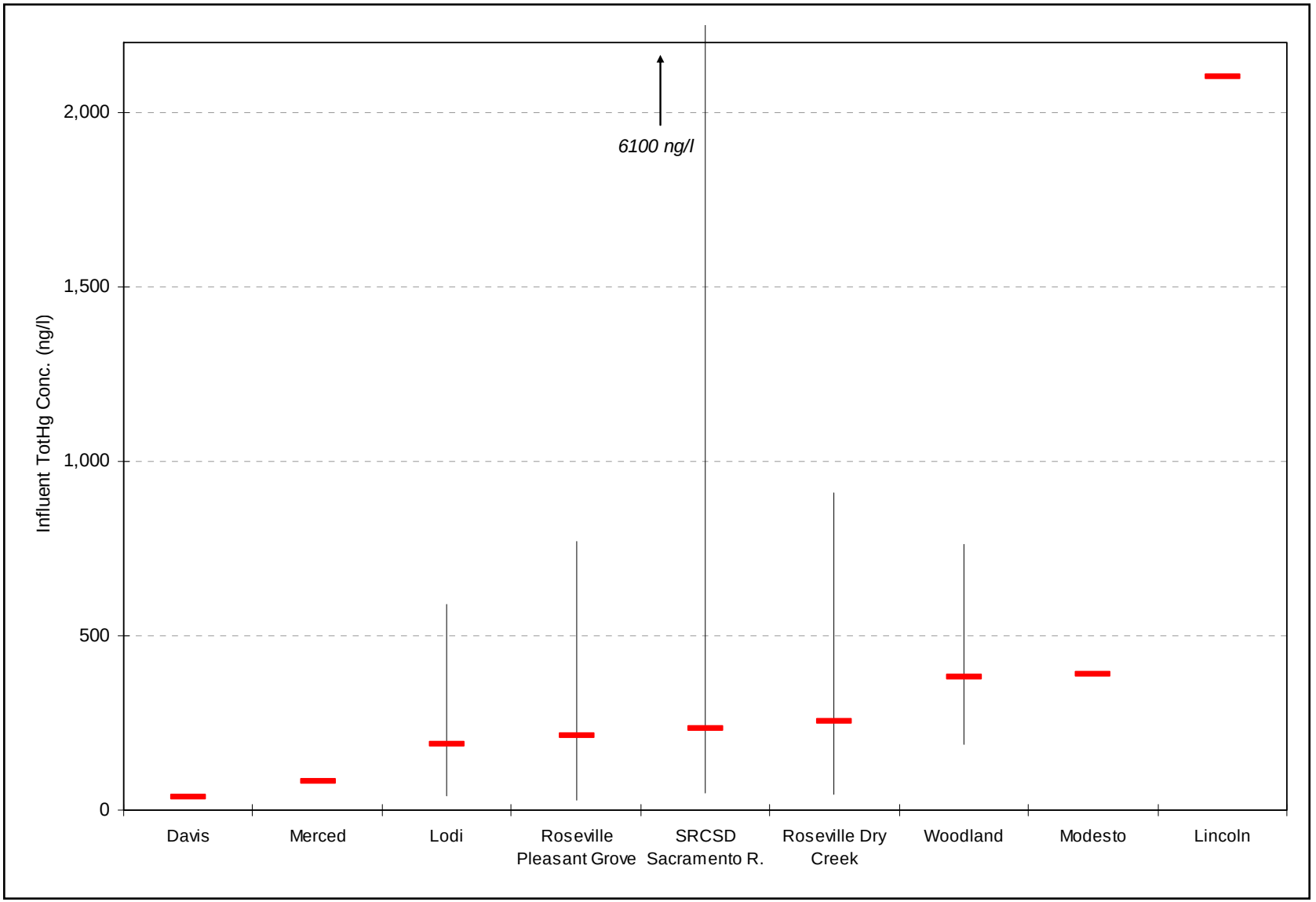

Figure 19: Average and Range of Influent Inorganic Mercury Concentrations for Each Municipal WWTP

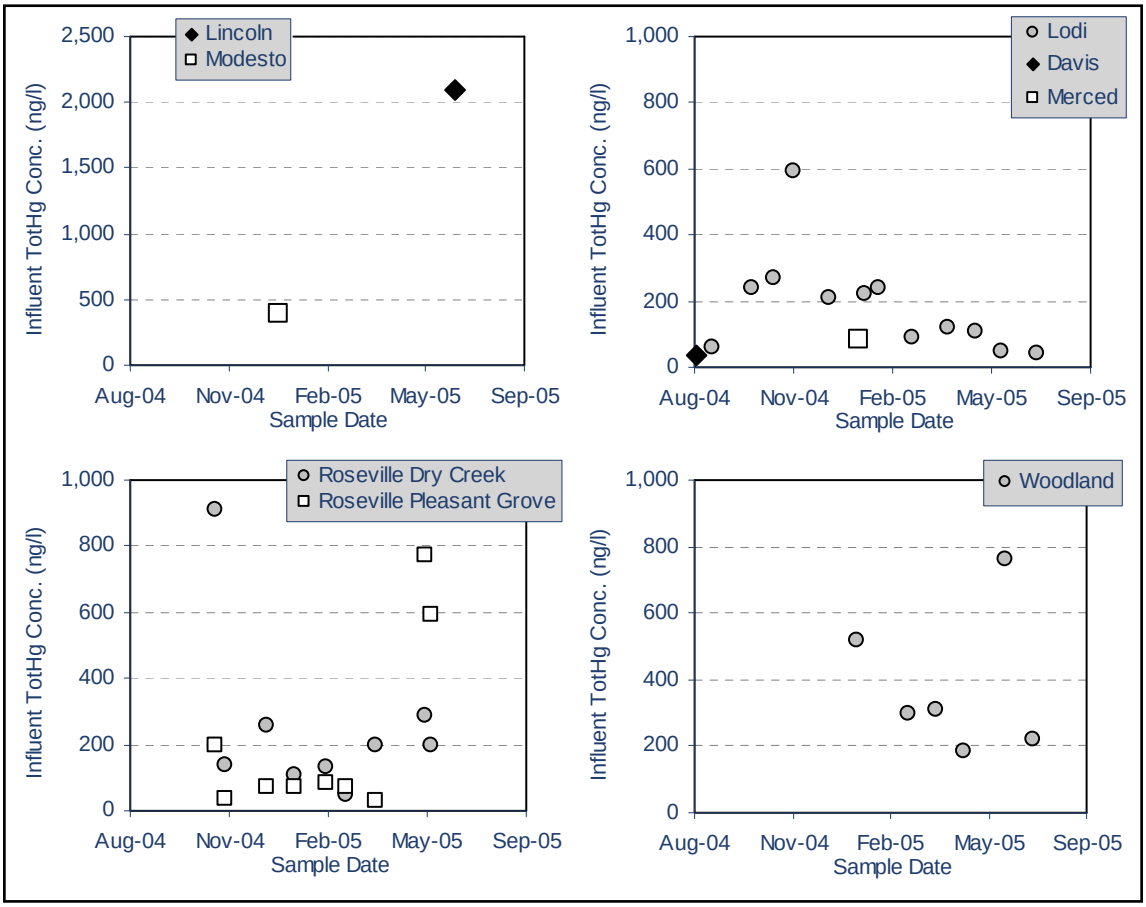

Figure 20: Time-series Graphs of Municipal WWTP Influent Inorganic Mercury Concentrations

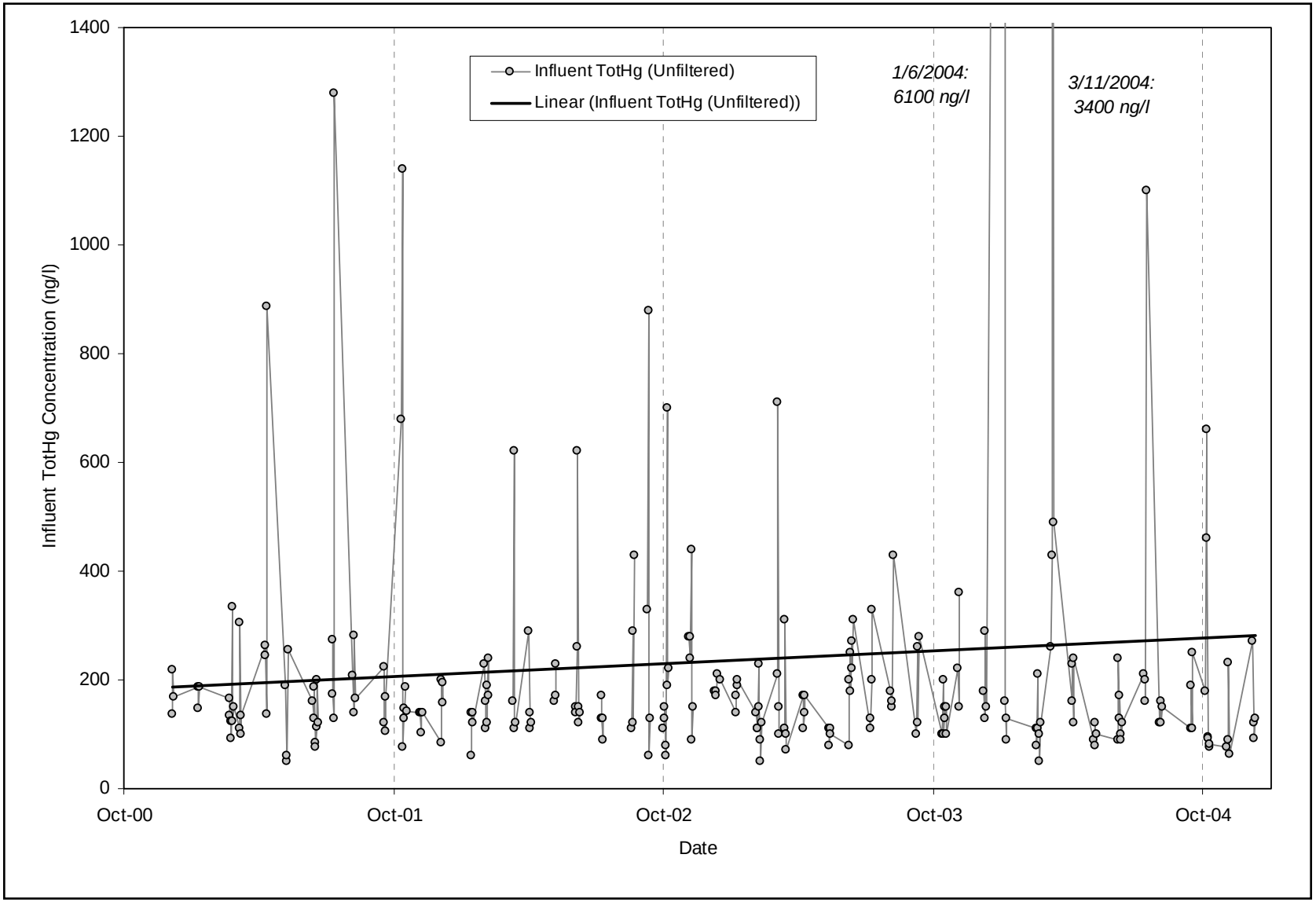

Figure 21: Time-series Graph of SRCSD Sacramento River WWTP Influent Inorganic Mercury Concentrations

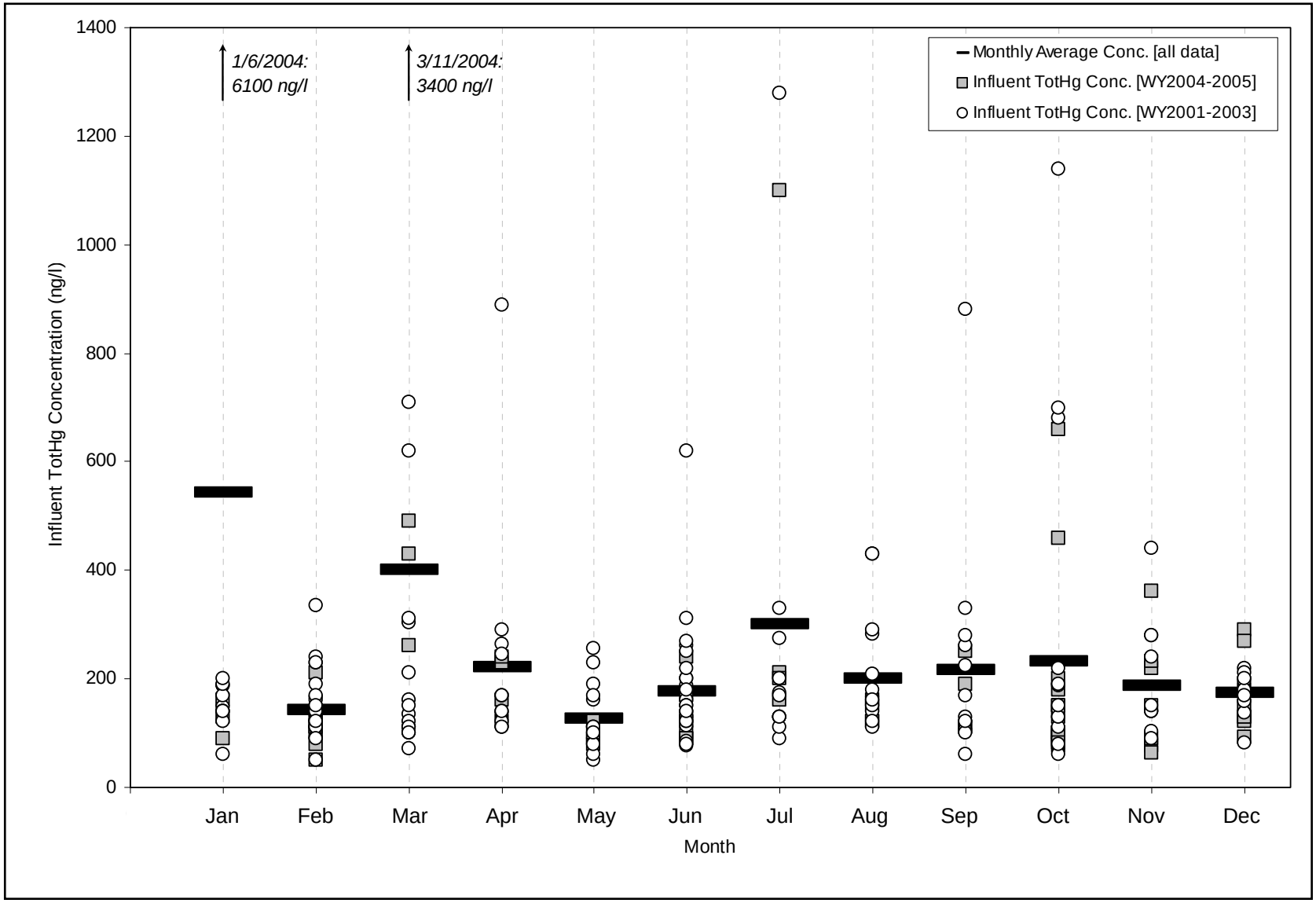

Figure 22: Monthly Influent Inorganic Mercury Concentrations for the SRCSD Sacramento River WWTP from December 2000 – December 2004

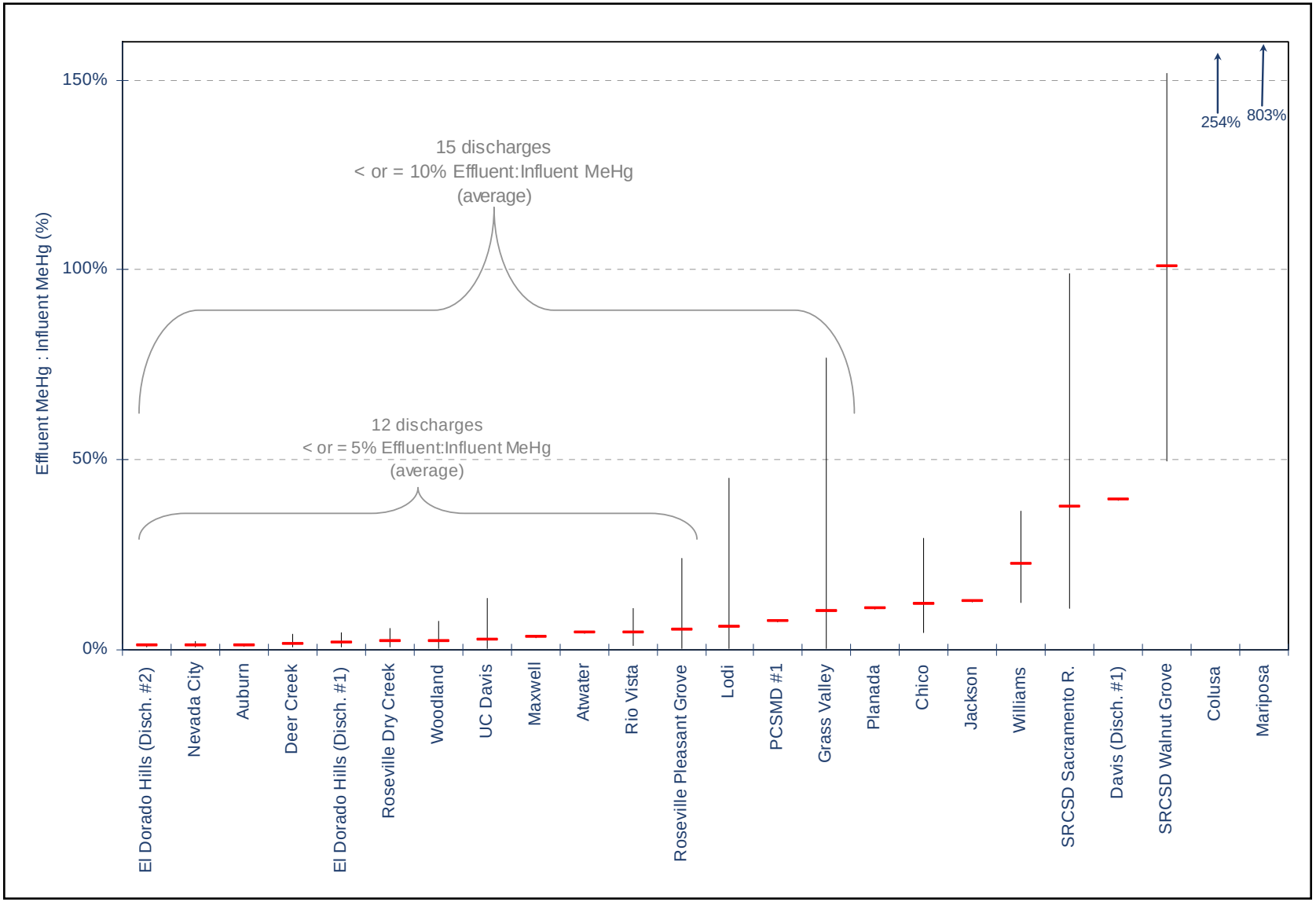

Figure 23: Average and Range of Effluent:Influent Methylmercury Concentration Ratios for Each Municipal WWTP

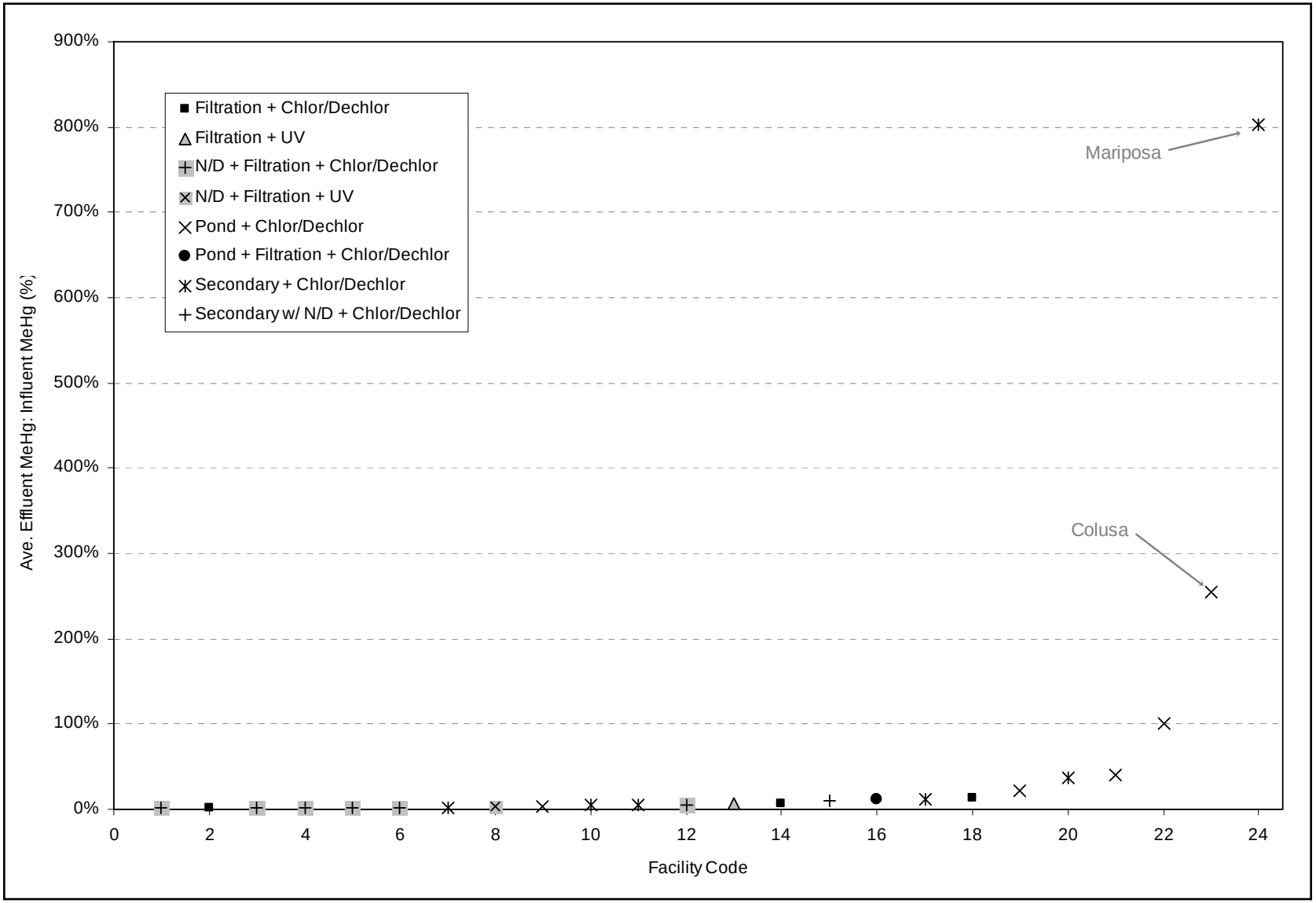

Figure 24: Average of Effluent:Influent Methylmercury Concentration Ratios with the Secondary Treatment Category Defined for Each Municipal WWTP

Facility Codes Used in Figure 24

Facility Code	NPDES No.	Facility
1	CA0078671	El Dorado Hills WWTP (Discharge 2)
2	CA0079901	Nevada City WWTP
3	CA0077712	Auburn WWTP
4	CA0078662	Deer Creek WWTP
5	CA0078671	El Dorado Hills WWTP (Discharge 1)
6	CA0079502	Roseville Dry Creek WWTP
7	CA0077950	Woodland WWTP
8	CA0077895	UC Davis WWTP
9	CA0079987	Maxwell PUD WWTP
10	CA0079197	Atwater WWTP
11	CA0079588	Rio Vista Main WWTP
12	CA0084573	Roseville Pleasant Grove WWTP
13	CA0079243	Lodi White Slough WWTP
14	CA0079316	Placer Co. SMD #1 WWTP
15	CA0079898	Grass Valley WWTP
16	CA0078950	Planada Comm. Service Dist. WWTP
17	CA0079081	Chico Regional WWTP
18	CA0079391	Jackson WWTP
19	CA0077933	Williams WWTP
20	CA0077682	SRCSD Sacramento River WWTP
21	CA0079049	Davis WWTP (Discharge 1)
22	CA0078794	SRCSD Walnut Grove WWTP (CSD1)
23	CA0078999	Colusa WWTP
24	CA0079430	Mariposa PUD WWTP

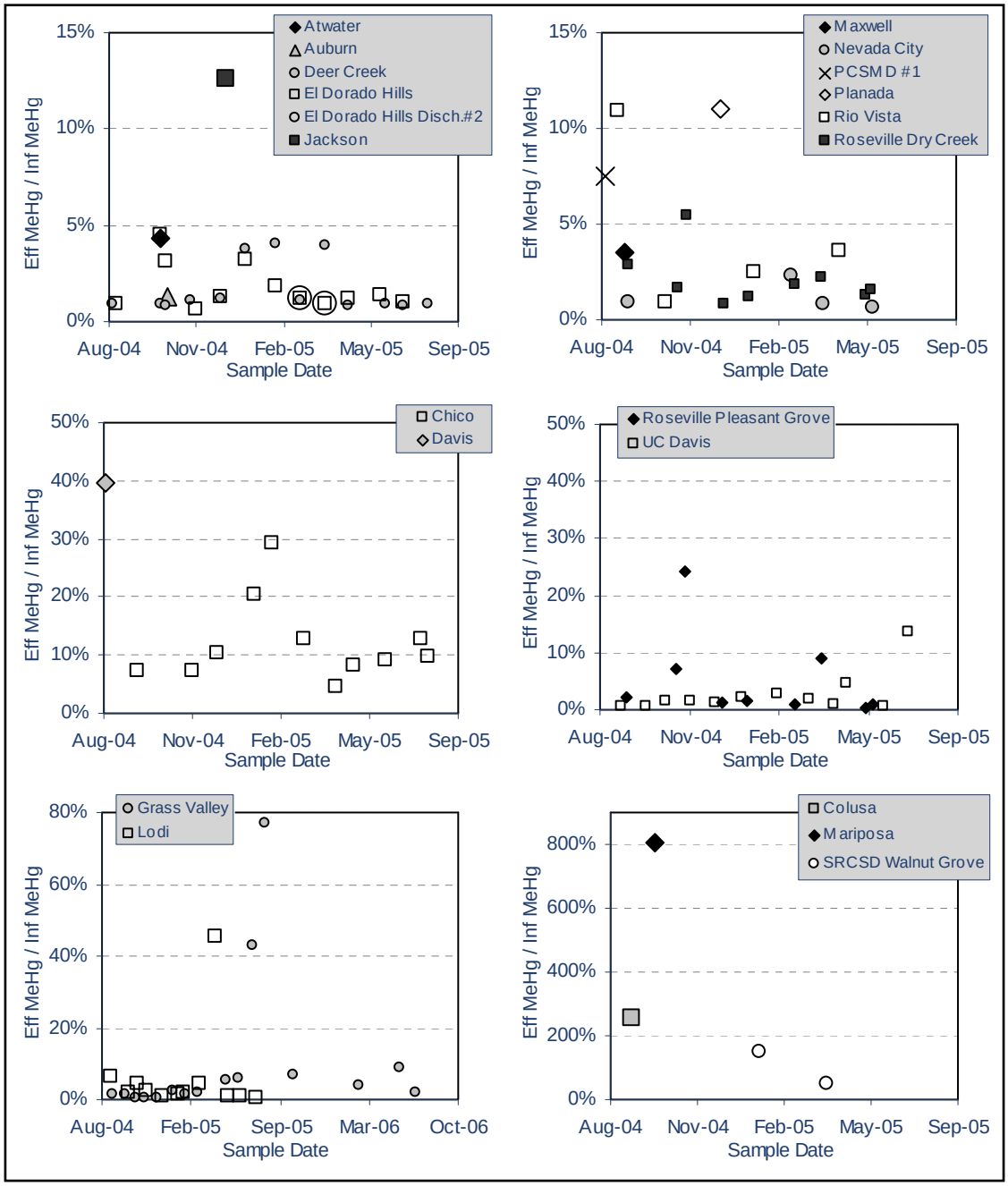

Figure 25: Time-series Graphs of Municipal WWTP Effluent:Influent Methylmercury Concentration Ratios

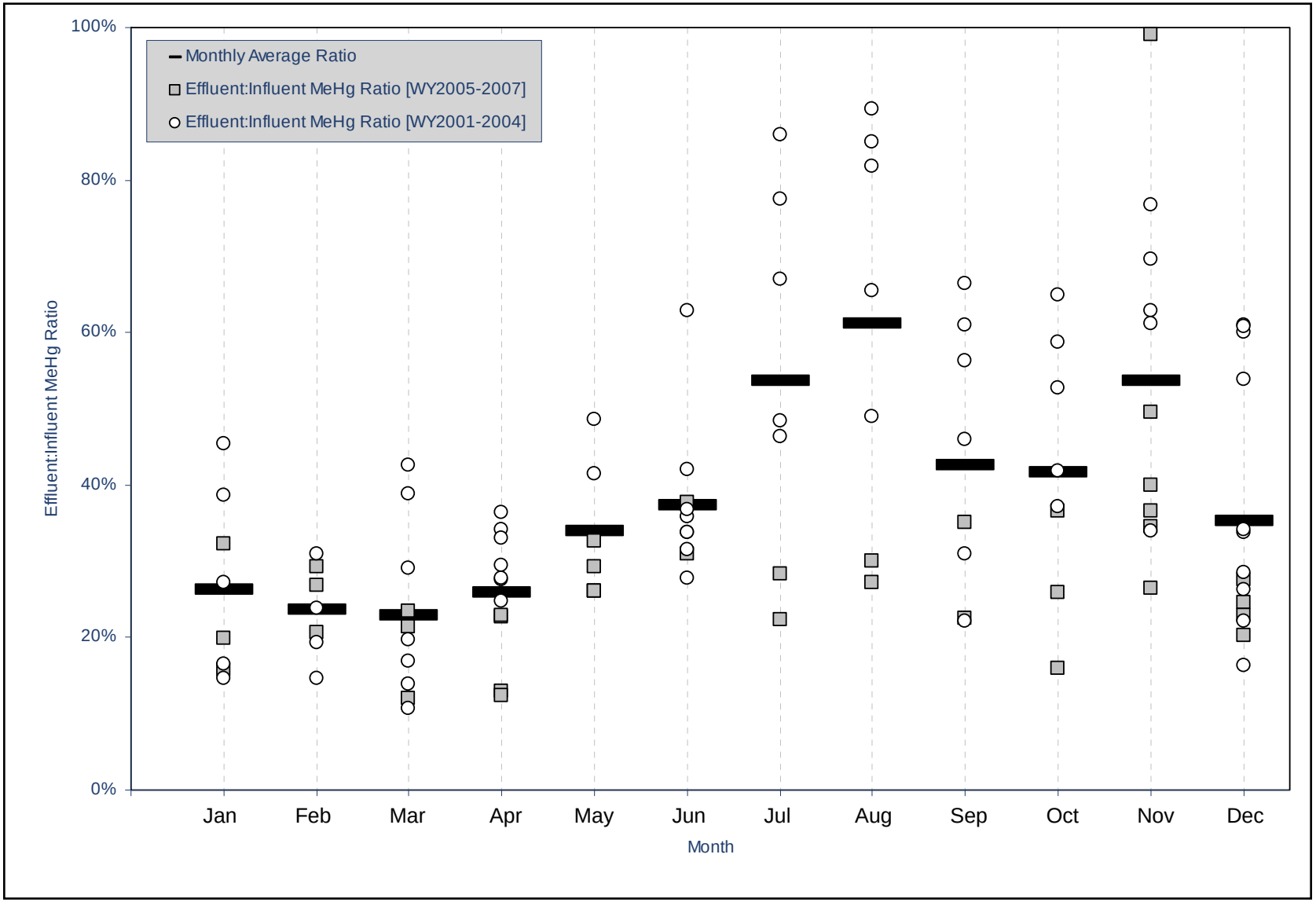

Figure 26: Monthly Effluent:Influent Methylmercury Concentration Ratios for the SRCSD Sacramento River WWTP from WY2001-2007

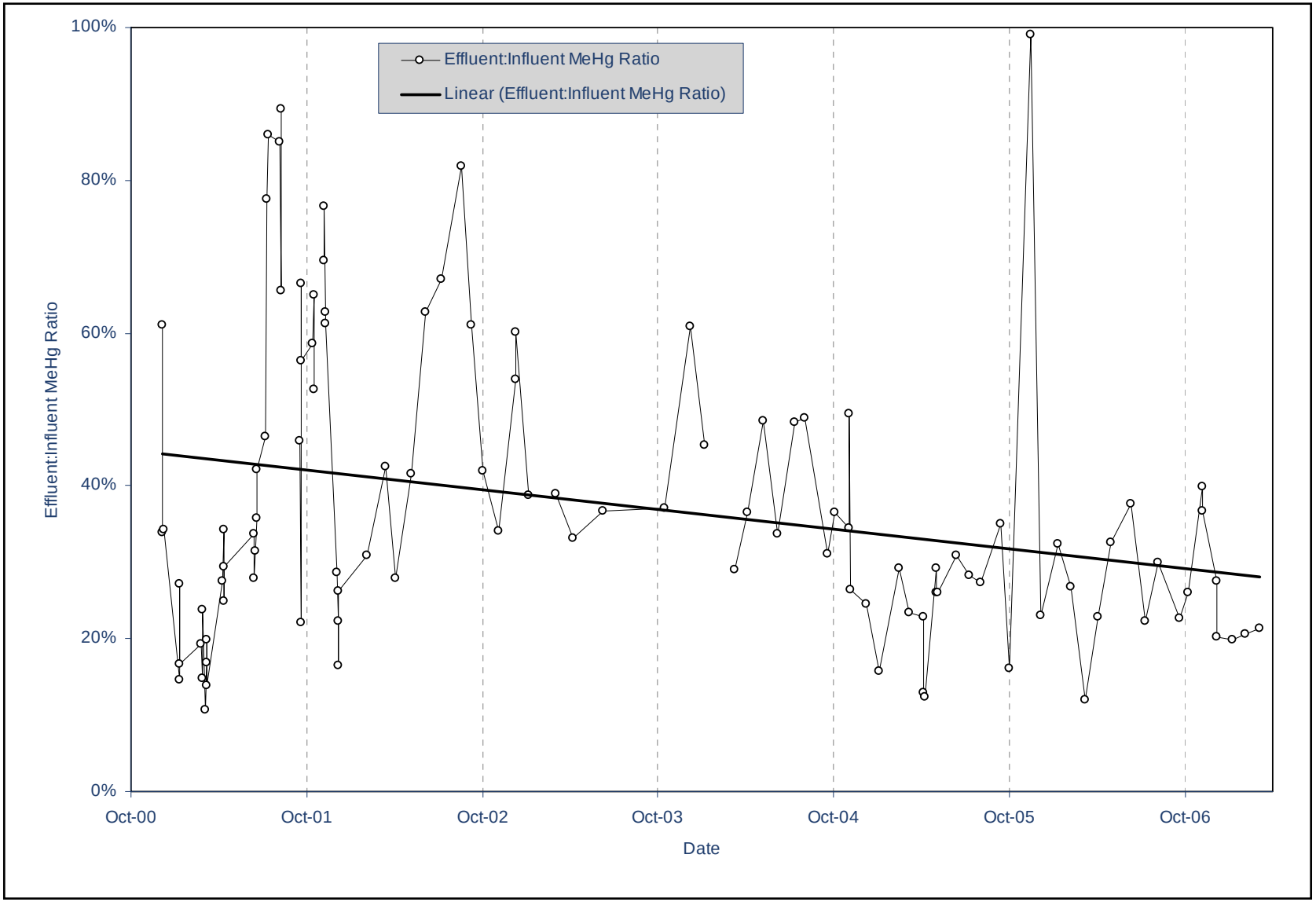

Figure 27: Time-series Graph of SRCSD Sacramento River WWTP Effluent:Influent Methylmercury Concentration Ratios

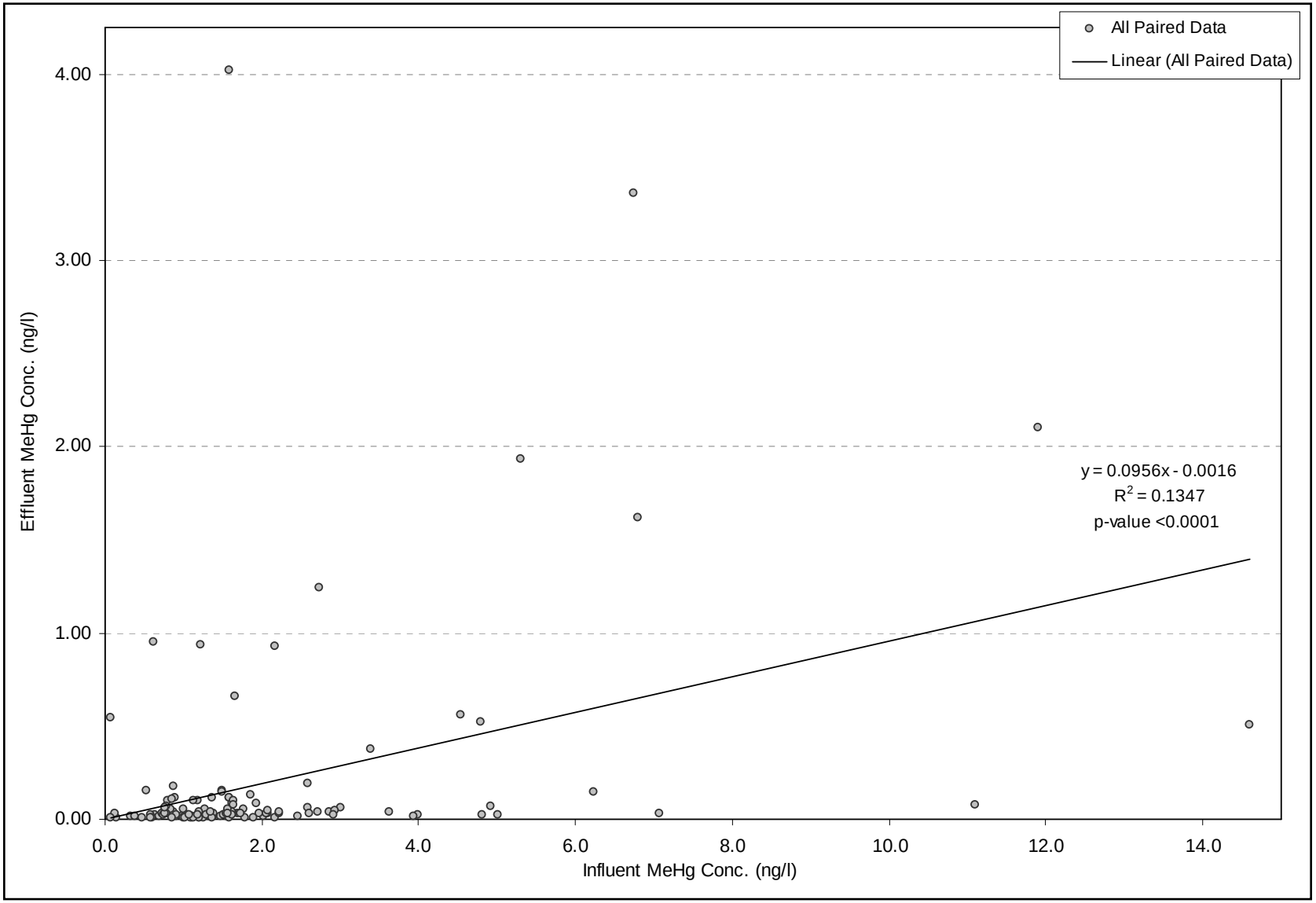

Figure 28a: Scatter-plot of Municipal WWTP Influent versus Effluent Methylmercury Concentrations for All Paired Data [excluding SRCSD Sacramento River WWTP data]

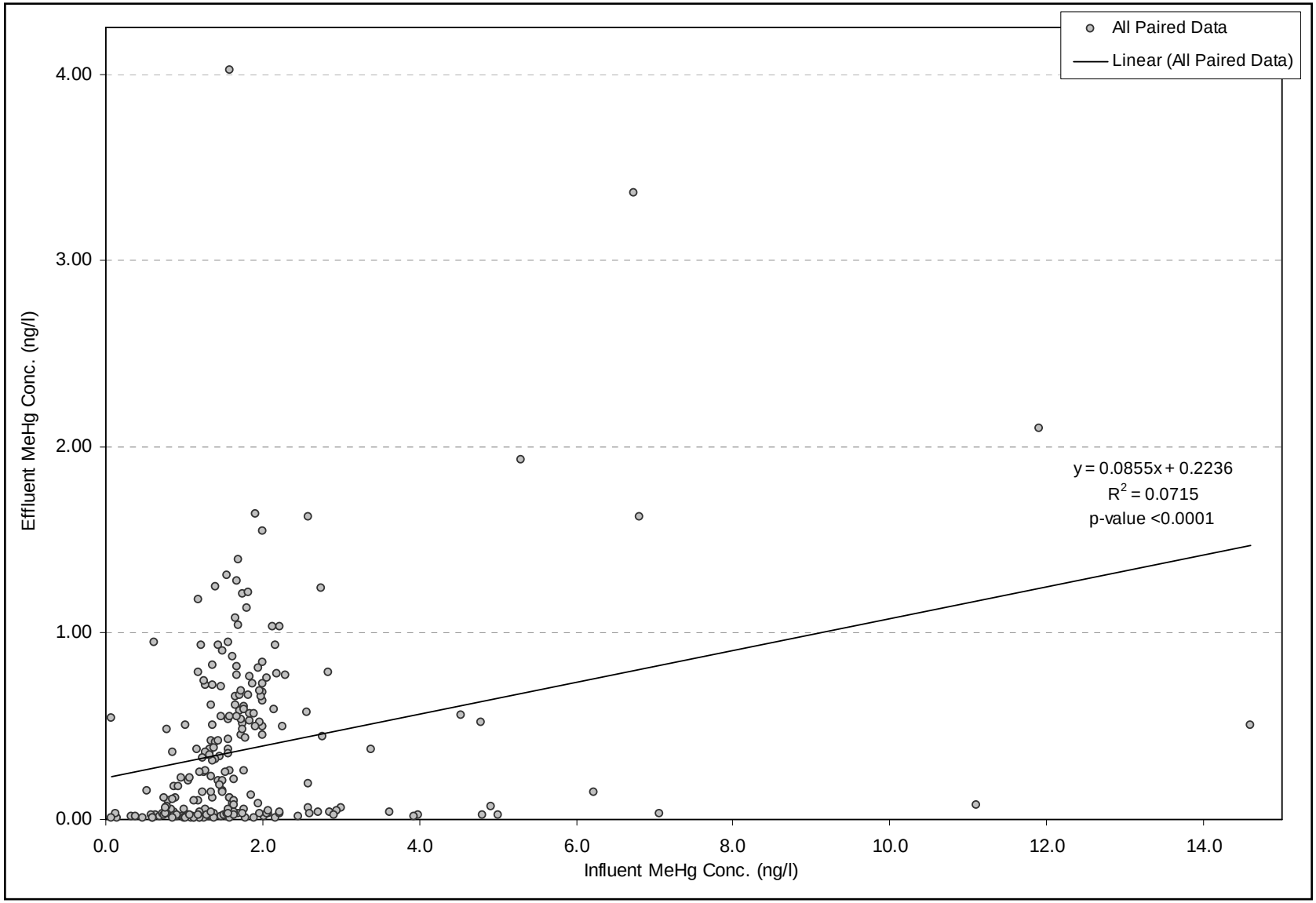

Figure 28b: Scatter-plot of Municipal WWTP Influent versus Effluent Methylmercury Concentrations for All Paired Data [including SRCSD Sacramento River WWTP data]

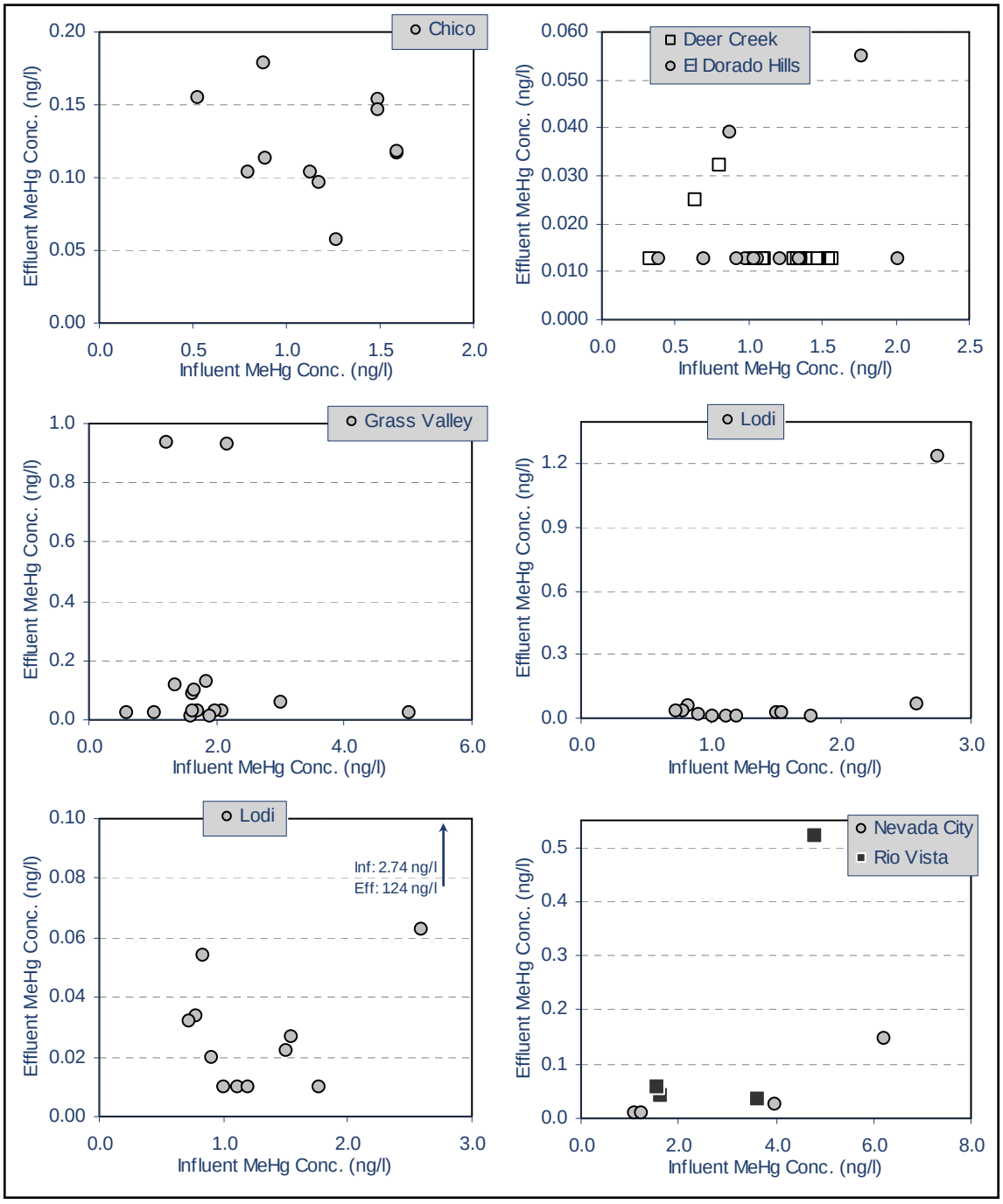

Figure 29a: Scatter-plots of Influent versus Effluent Methylmercury Concentrations for Each Municipal WWTP

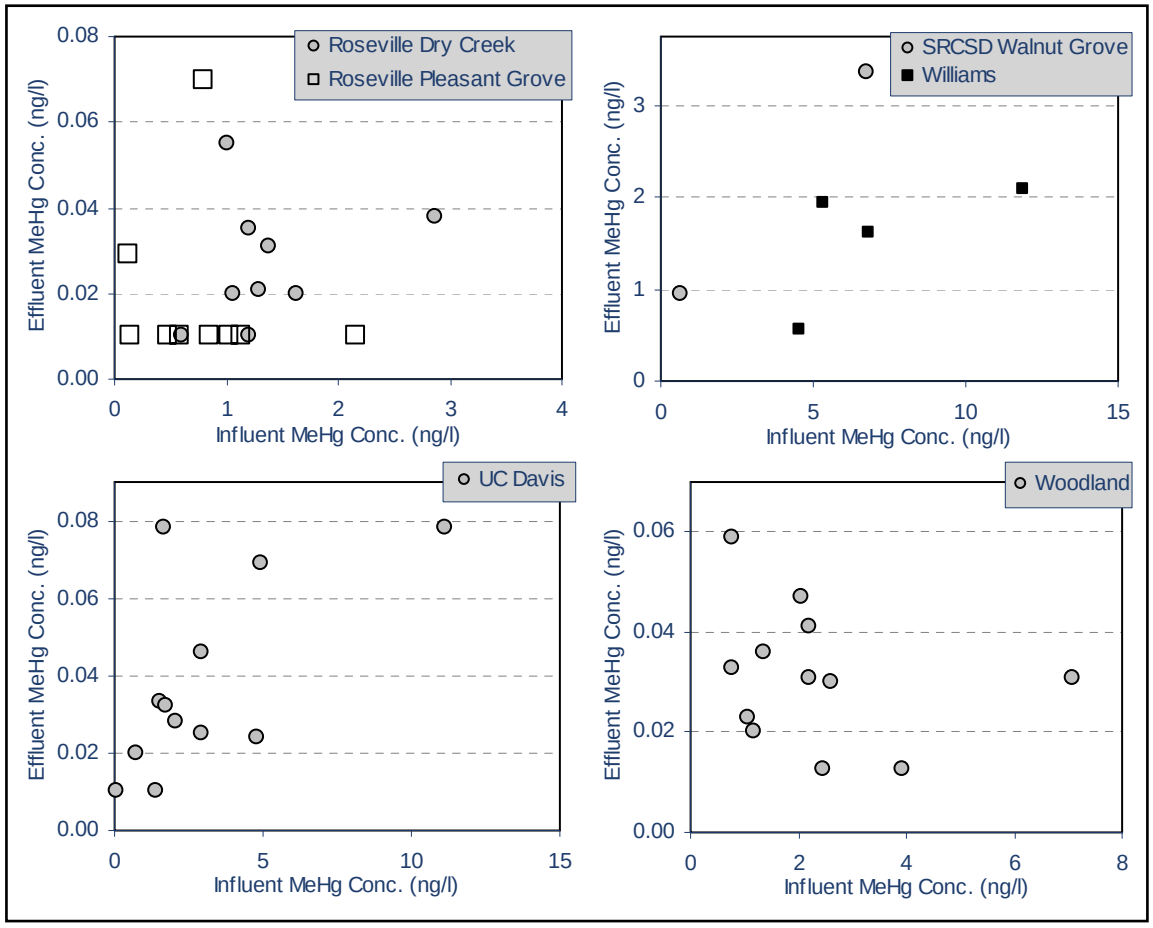

Figure 29b: Scatter-plots of Influent versus Effluent Methylmercury Concentrations for Each Municipal WWTP

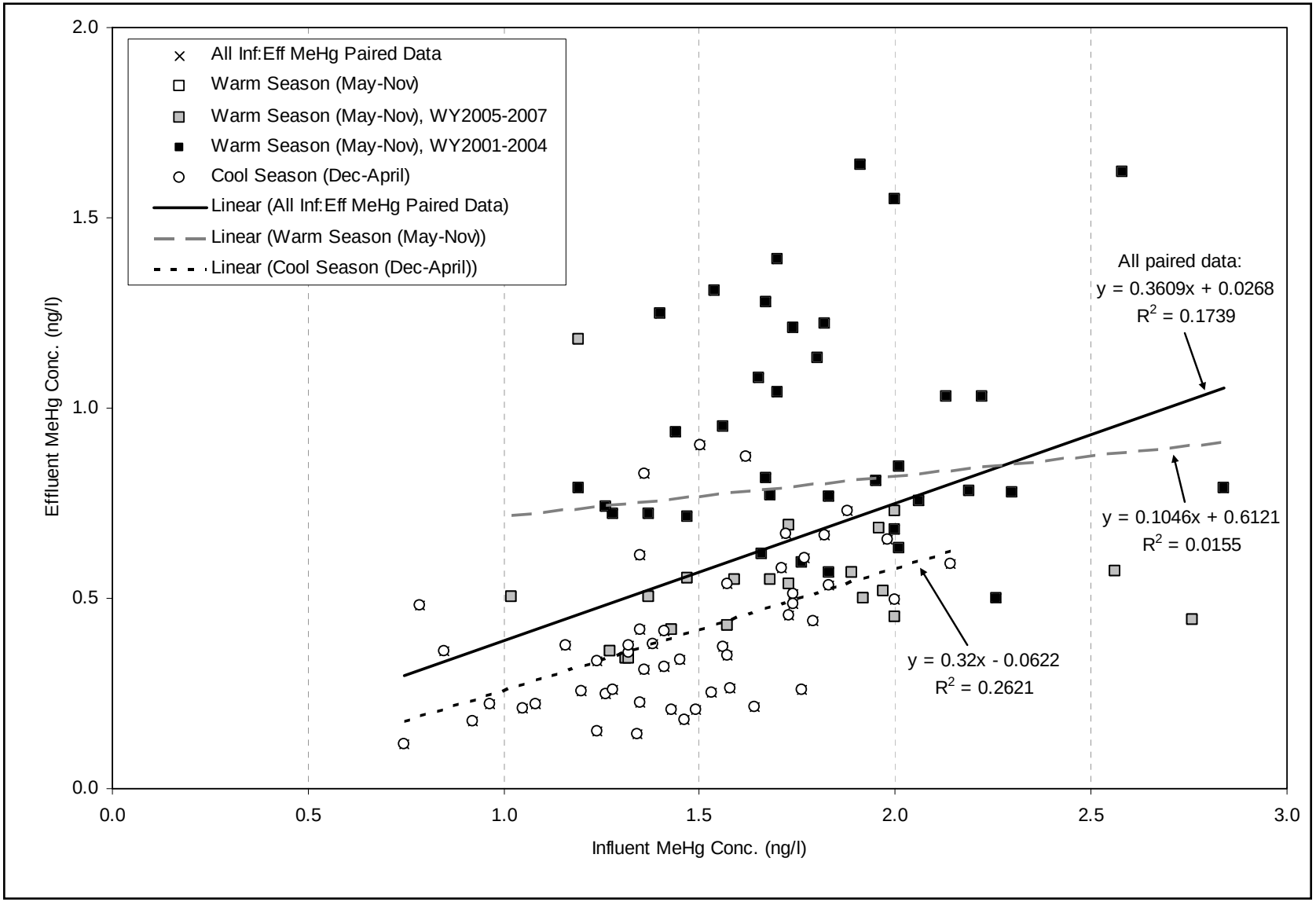

Figure 30: Scatter-plot of Influent versus Effluent Methylmercury Concentrations for the SRCSD Sacramento River WWTP

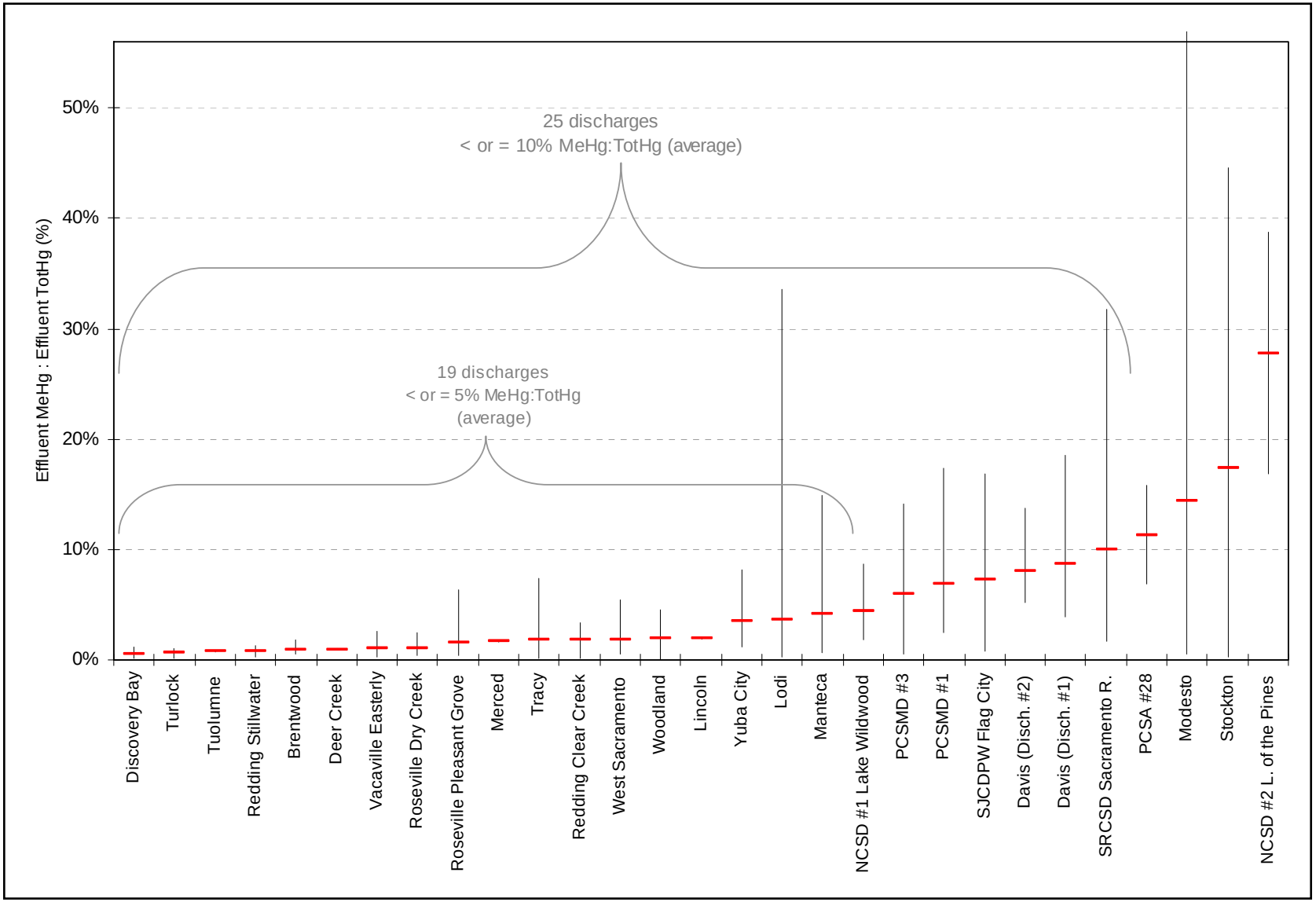

Figure 31: Average and Range of Effluent MeHg:TotHg Concentration Ratios for Each Municipal WWTP

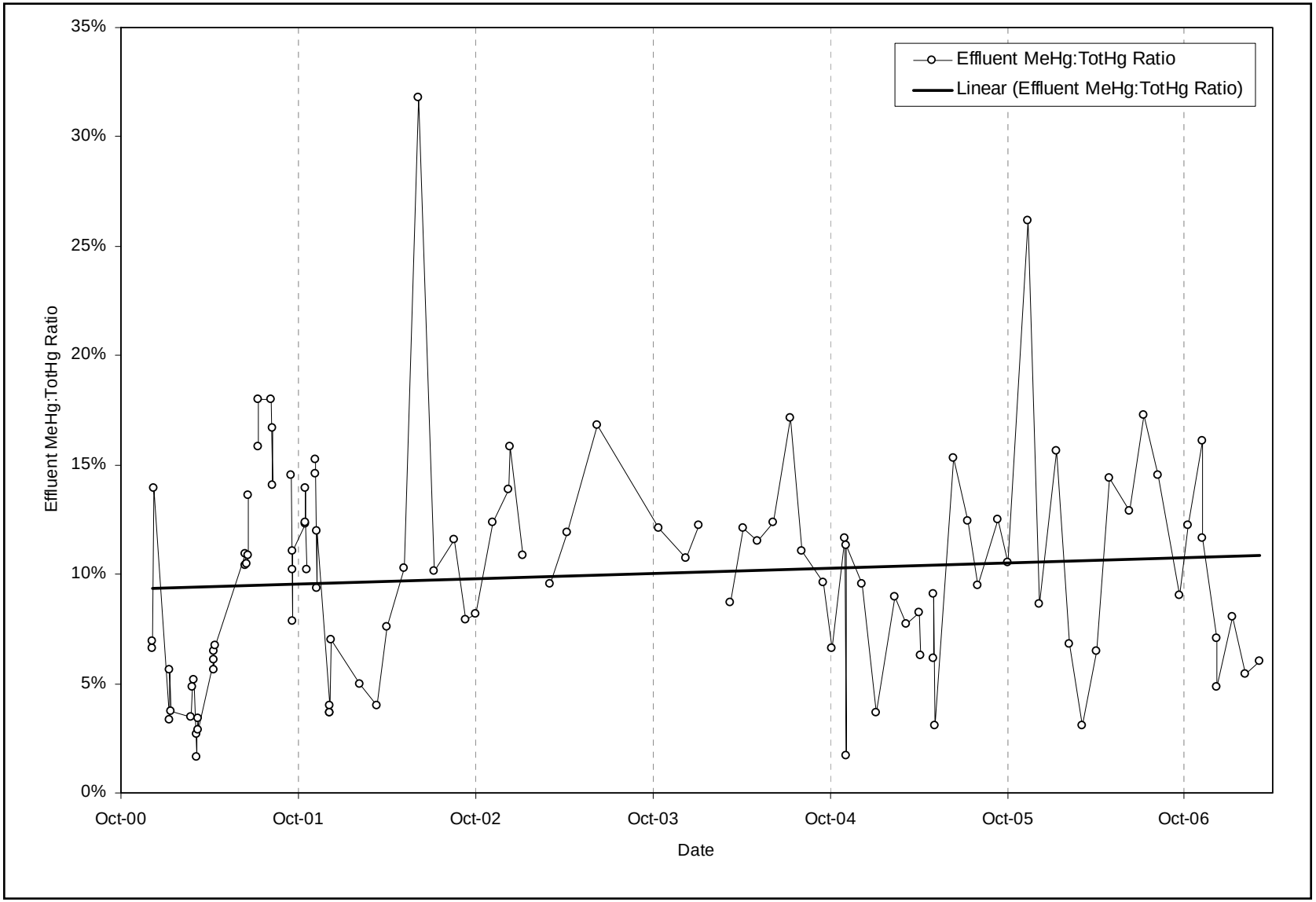

Figure 32: Time-series Graph of SRCSD Sacramento River WWTP Effluent MeHg:TotHg Concentration Ratios

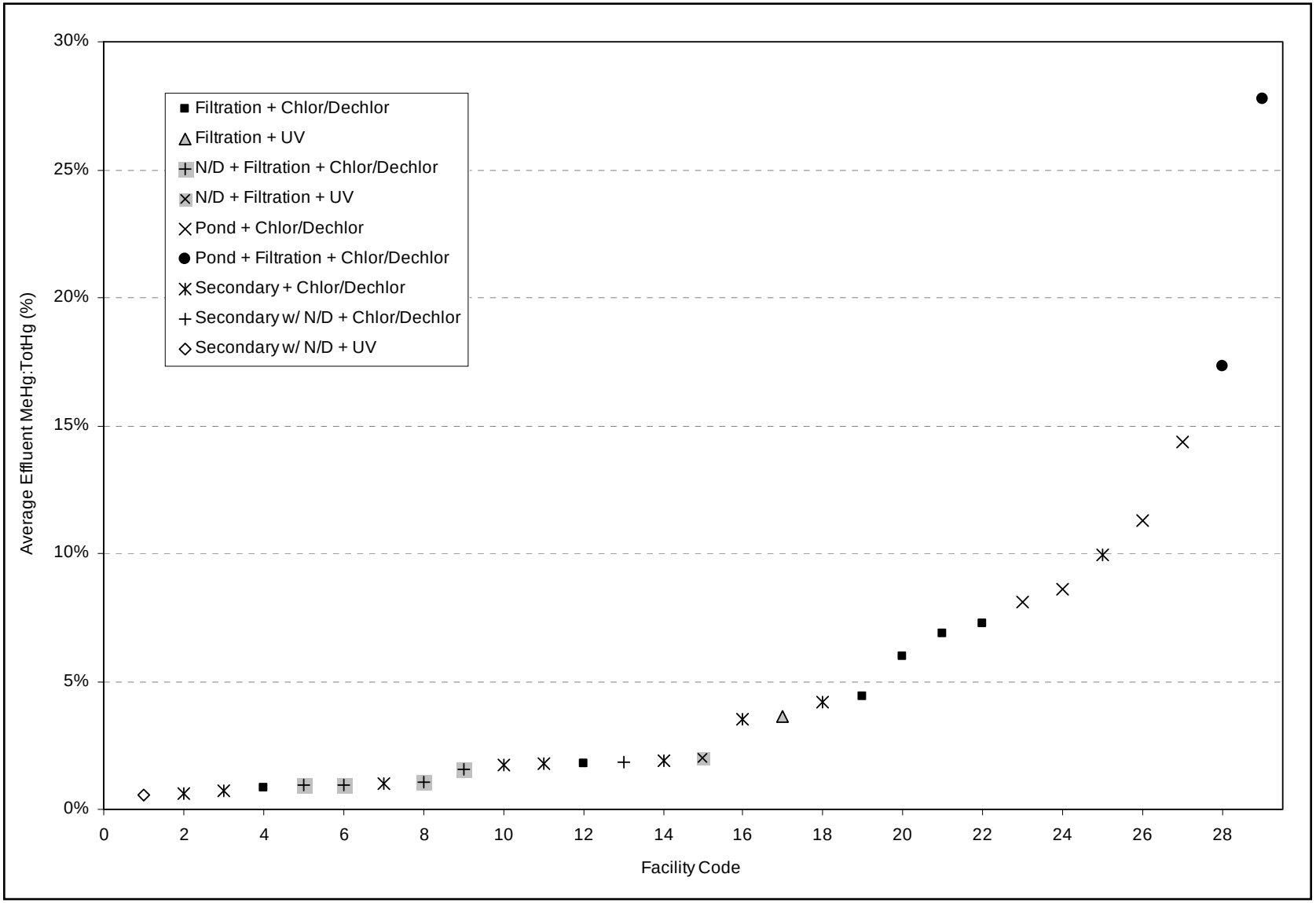

Figure 33: Average of Effluent MeHg:TotHg Concentration Ratios with the Secondary Treatment Category Defined for Each Municipal WWTP

Facility Codes Used in Figure 33

Facility Code	NPDES No.	Facility
1	CA0078590	Discovery Bay WWTP
2	CA0078948	Turlock WWTP
3	CA0084727	Tuolumne UD Sonora RWTP/ Jamestown SDWTP
4	CA0082589	Redding Stillwater WWTP
5	CA0082660	Brentwood WWTP
6	CA0078662	Deer Creek WWTP
7	CA0077691	Vacaville Easterly WWTP
8	CA0079502	Roseville Dry Creek WWTP
9	CA0084573	Roseville Pleasant Grove WWTP
10	CA0079219	Merced WWTP
11	CA0079154	Tracy WWTP
12	CA0079731	Redding Clear Creek WWTP
13	CA0079171	West Sacramento WWTP
14	CA0077950	Woodland WWTP
15	CA0084476	Lincoln WWTP
16	CA0079260	Yuba City WWTP
17	CA0079243	Lodi White Slough WWTP
18	CA0081558	Manteca WWTP
19	CA0077828	Nevada Co SD #1 Lake Wildwood WWTP
20	CA0079367	Placer Co. SMD #3 WWTP
21	CA0079316	Placer Co. SMD #1 WWTP
22	CA0082848	San Joaquin Co DPW - Flag City WWTP
23	CA0079049	Davis WWTP (Discharge 2)
24	CA0079049	Davis WWTP (Discharge 1)
25	CA0077682	SRCSD Sacramento River WWTP
26	CA0079341	Placer Co. SA #28 Zone #6 WWTP
27	CA0079103	Modesto WWTP
28	CA0079138	Stockton WWTP
29	CA0081612	Nevada Co SD #2 Lake of the Pines WWTP

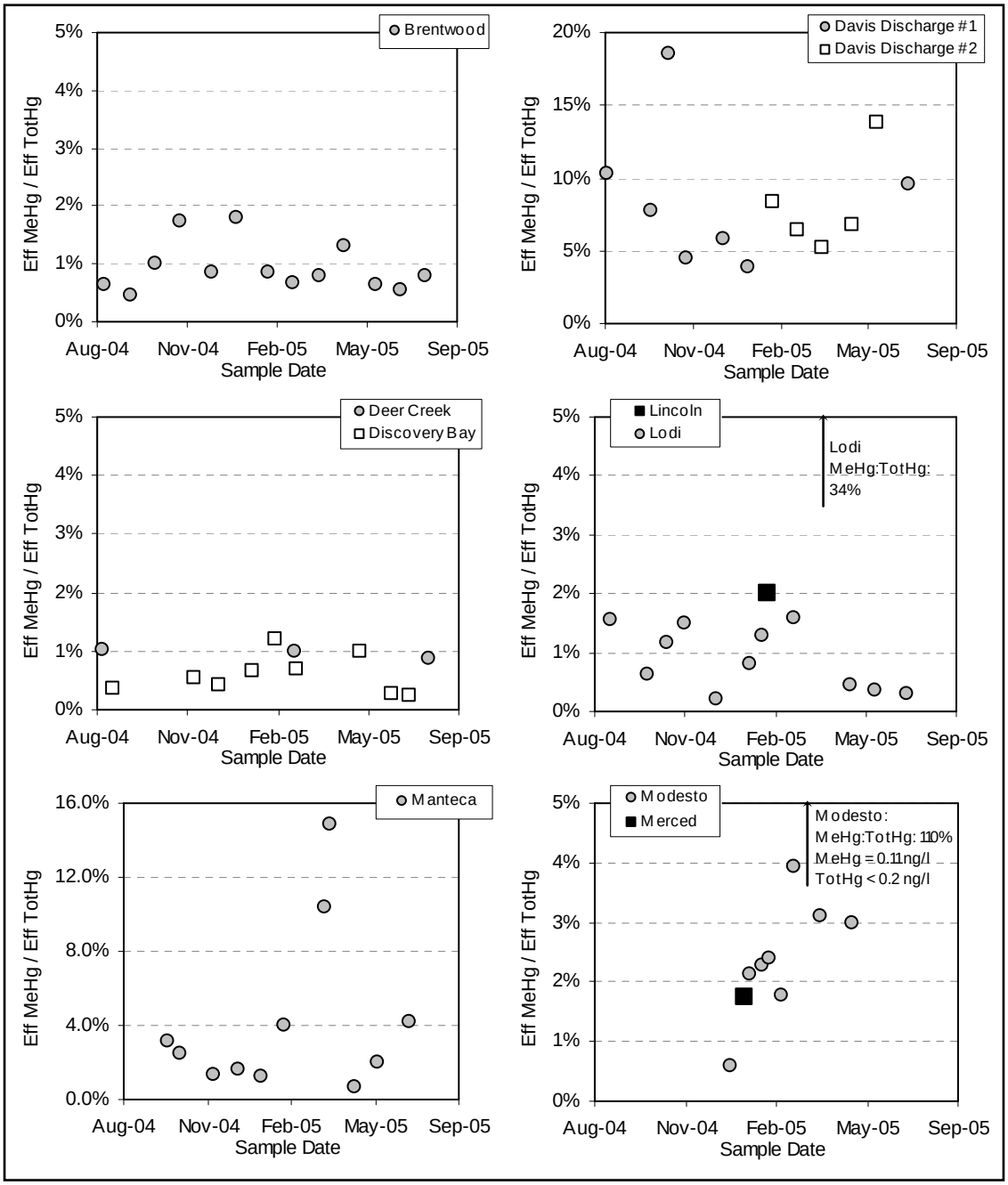

Figure 34a: Time-series Graphs of Municipal WWTP Effluent MeHg:TotHg Concentration Ratios

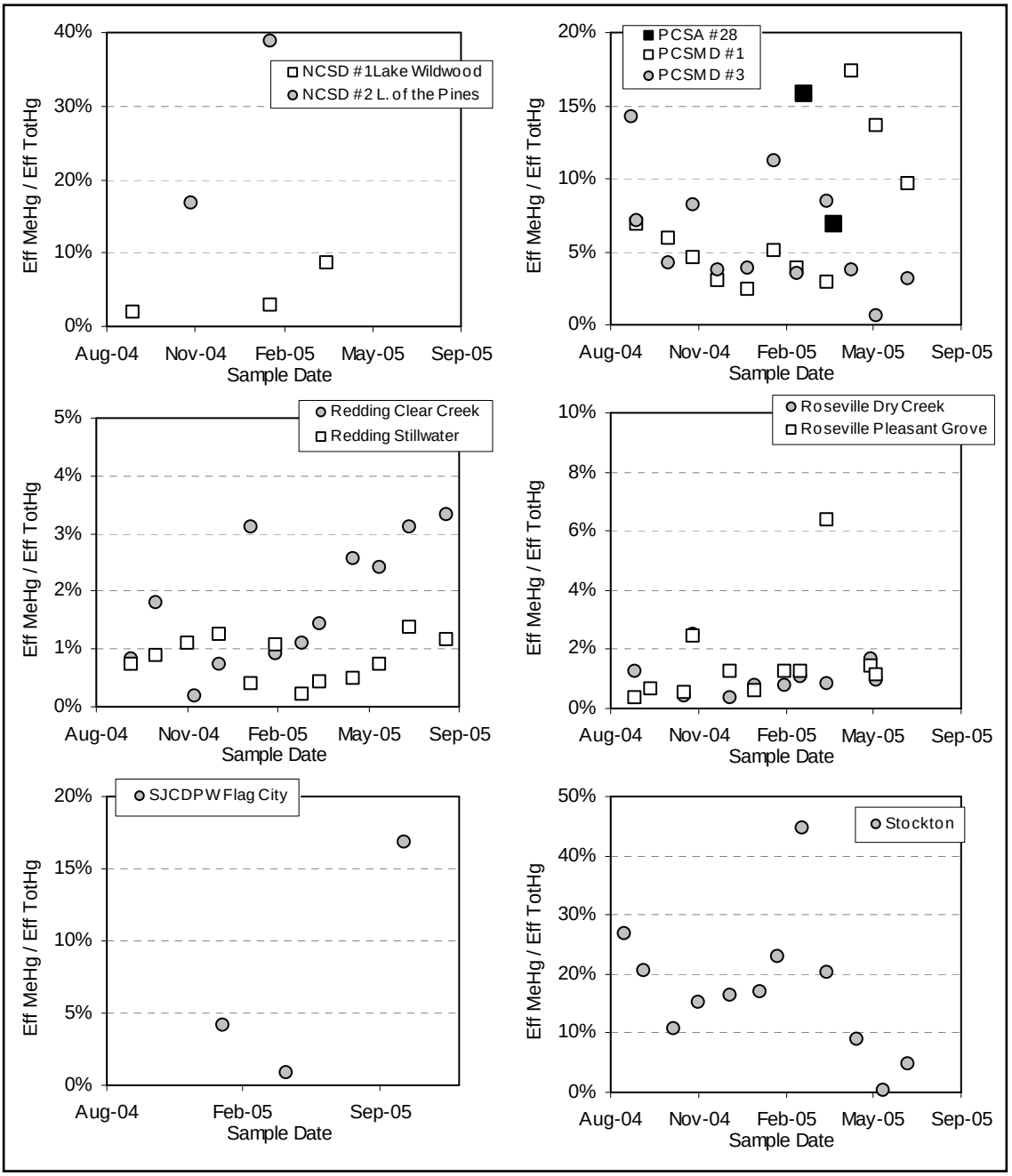

Figure 34b: Time-series Graphs of Municipal WWTP Effluent MeHg:TotHg Concentration Ratios

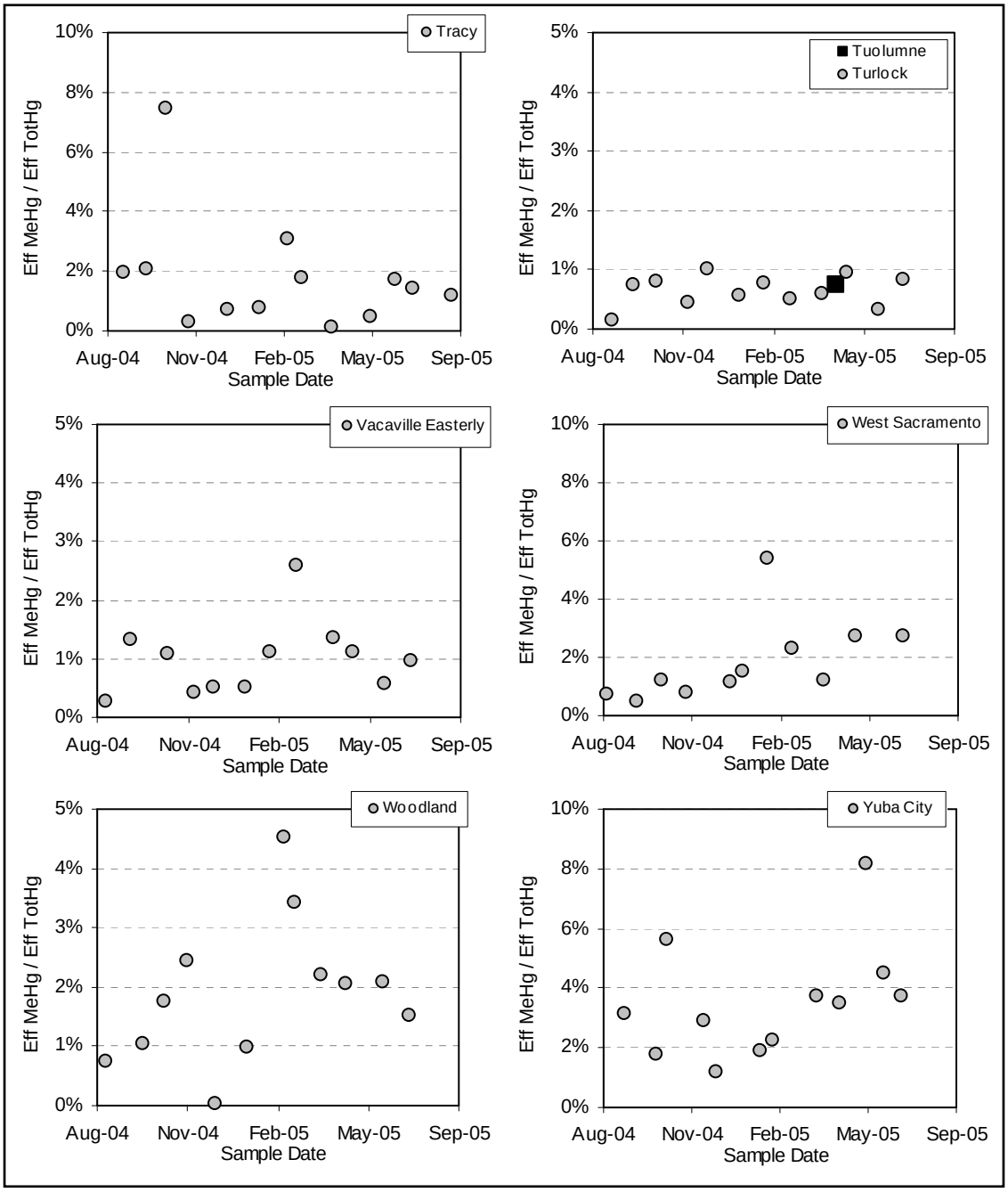

Figure 34c: Time-series Graphs of Municipal WWTP Effluent MeHg:TotHg Concentration Ratios

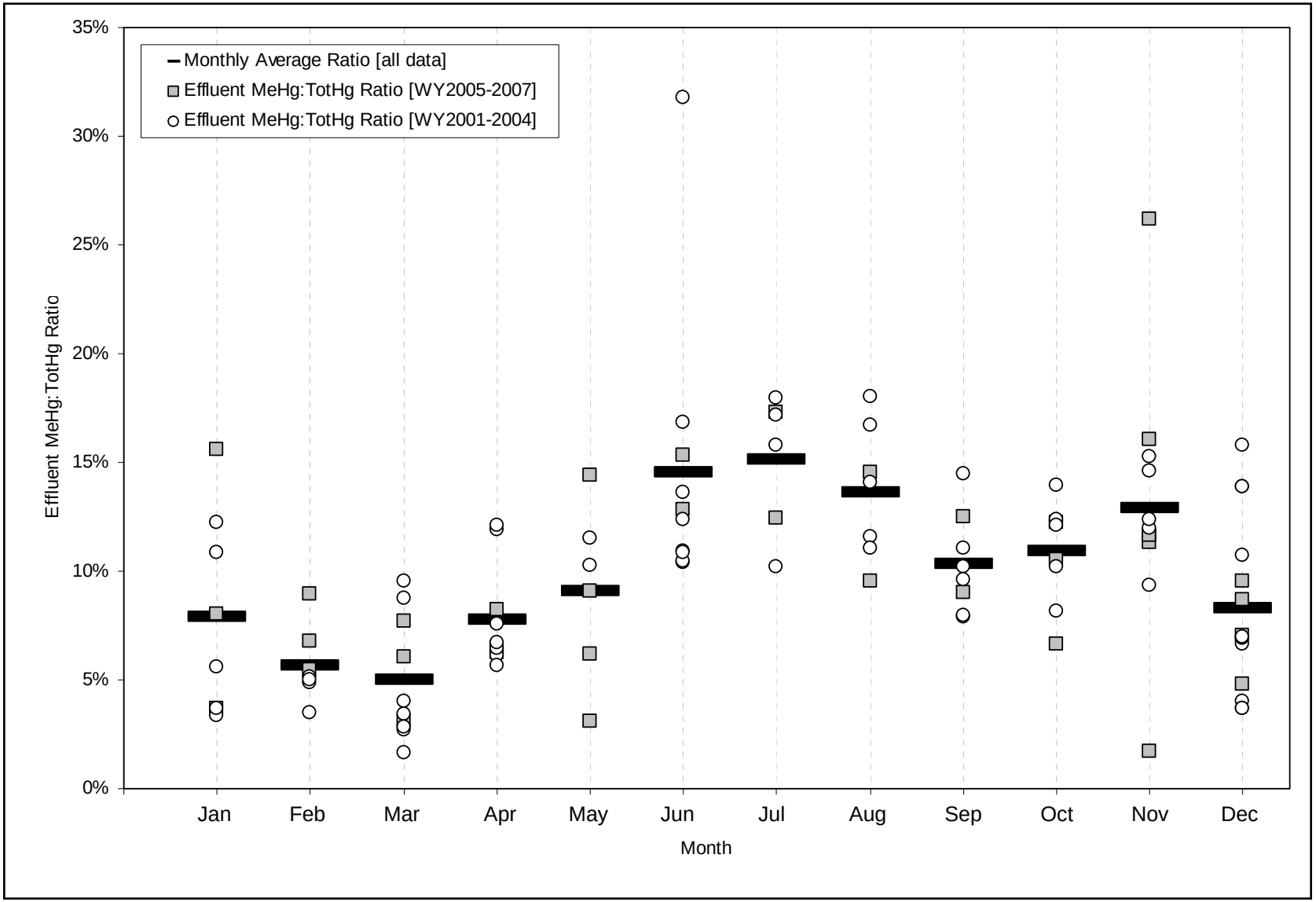

Figure 35: Monthly Effluent MeHg:TotHg Concentration Ratios for the SRCSD Sacramento River WWTP from WY2001-2007

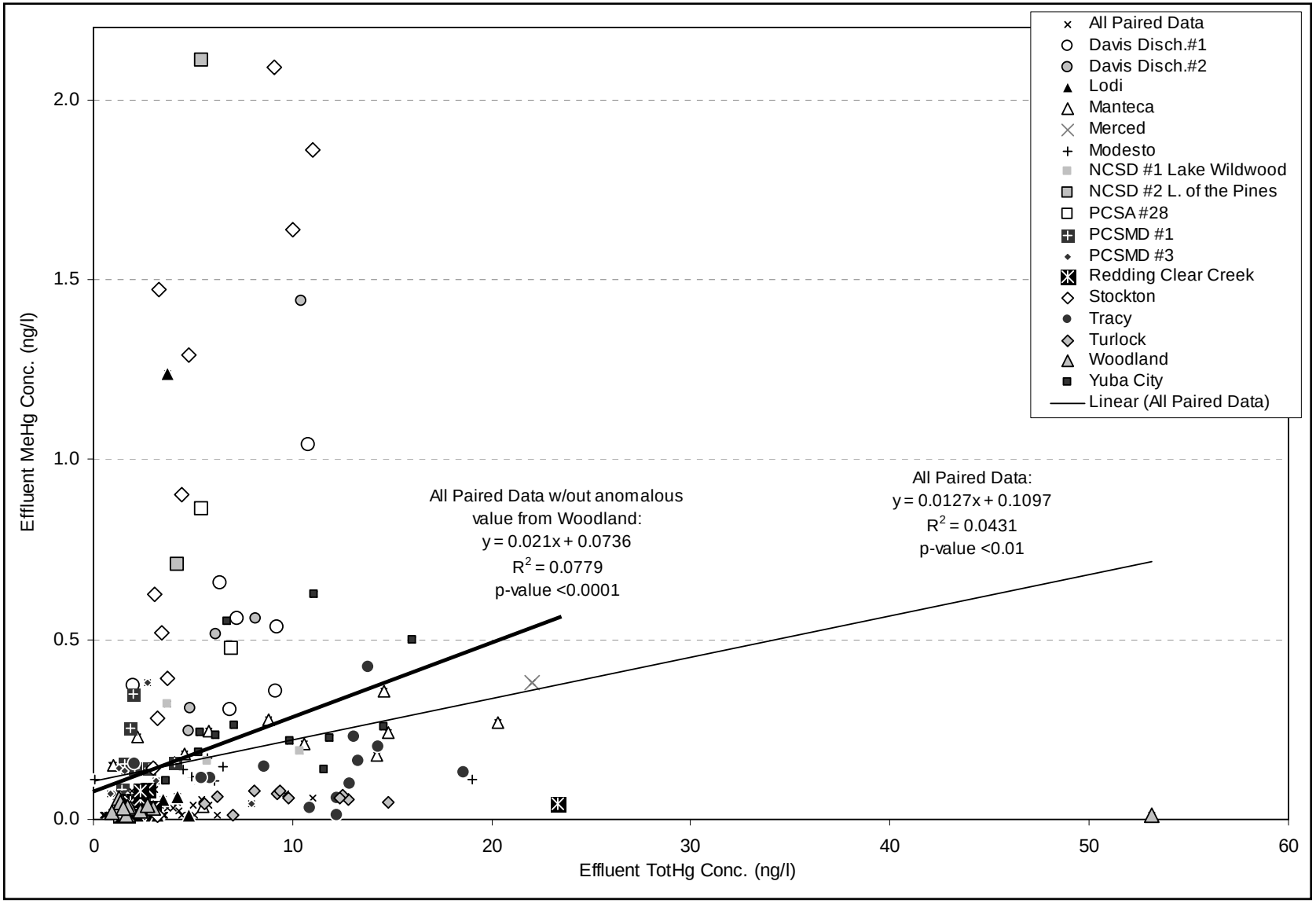

Figure 36a: Scatter-plot of Municipal WWTP Effluent Inorganic Mercury versus Effluent Methylmercury Concentrations for All Paired Data [excluding SRCSD Sacramento River WWTP data]

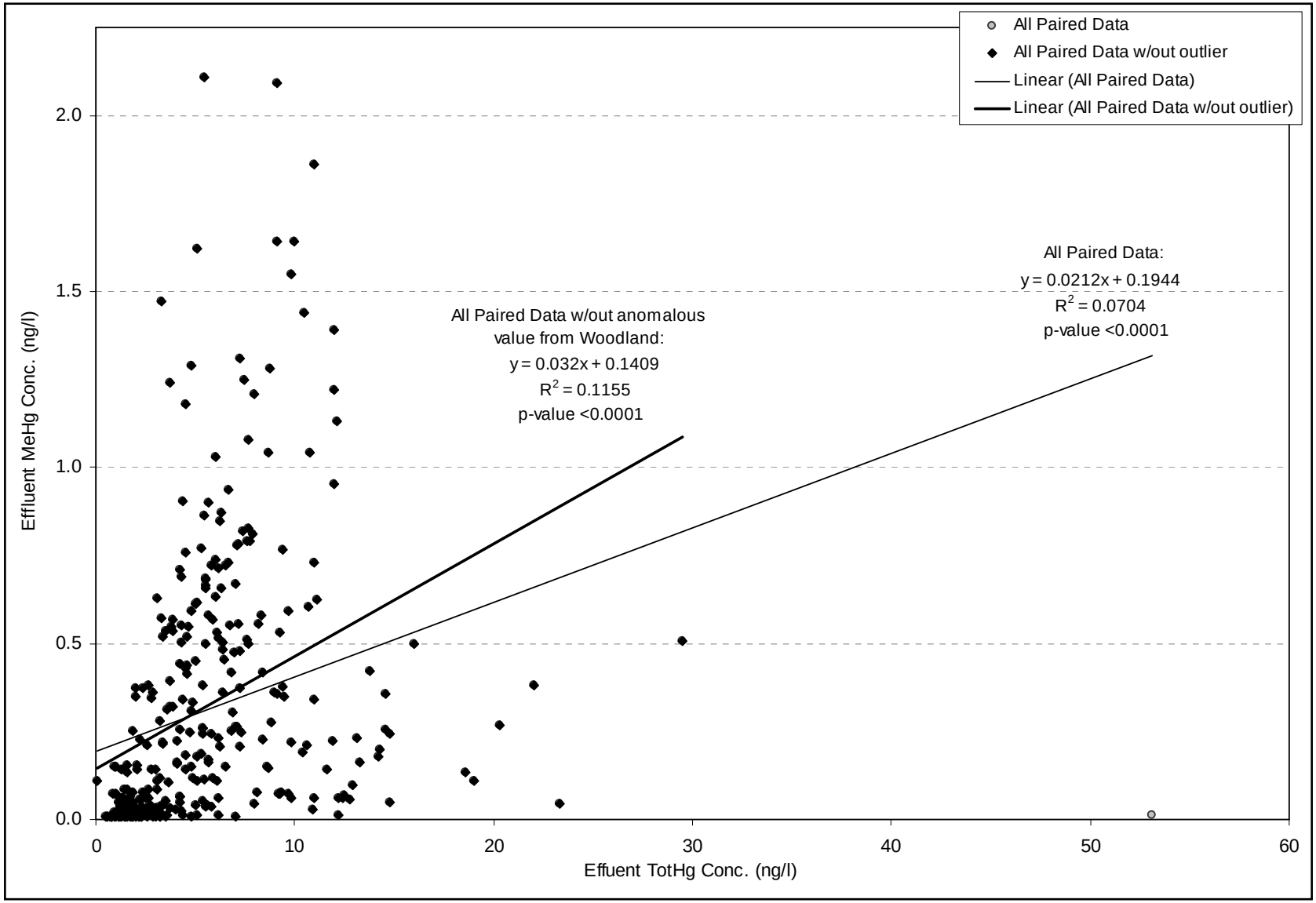

Figure 36b: Scatter-plot of Municipal WWTP Effluent Inorganic Mercury versus Effluent Methylmercury Concentrations for All Paired Data [including SRCSD Sacramento River WWTP data]

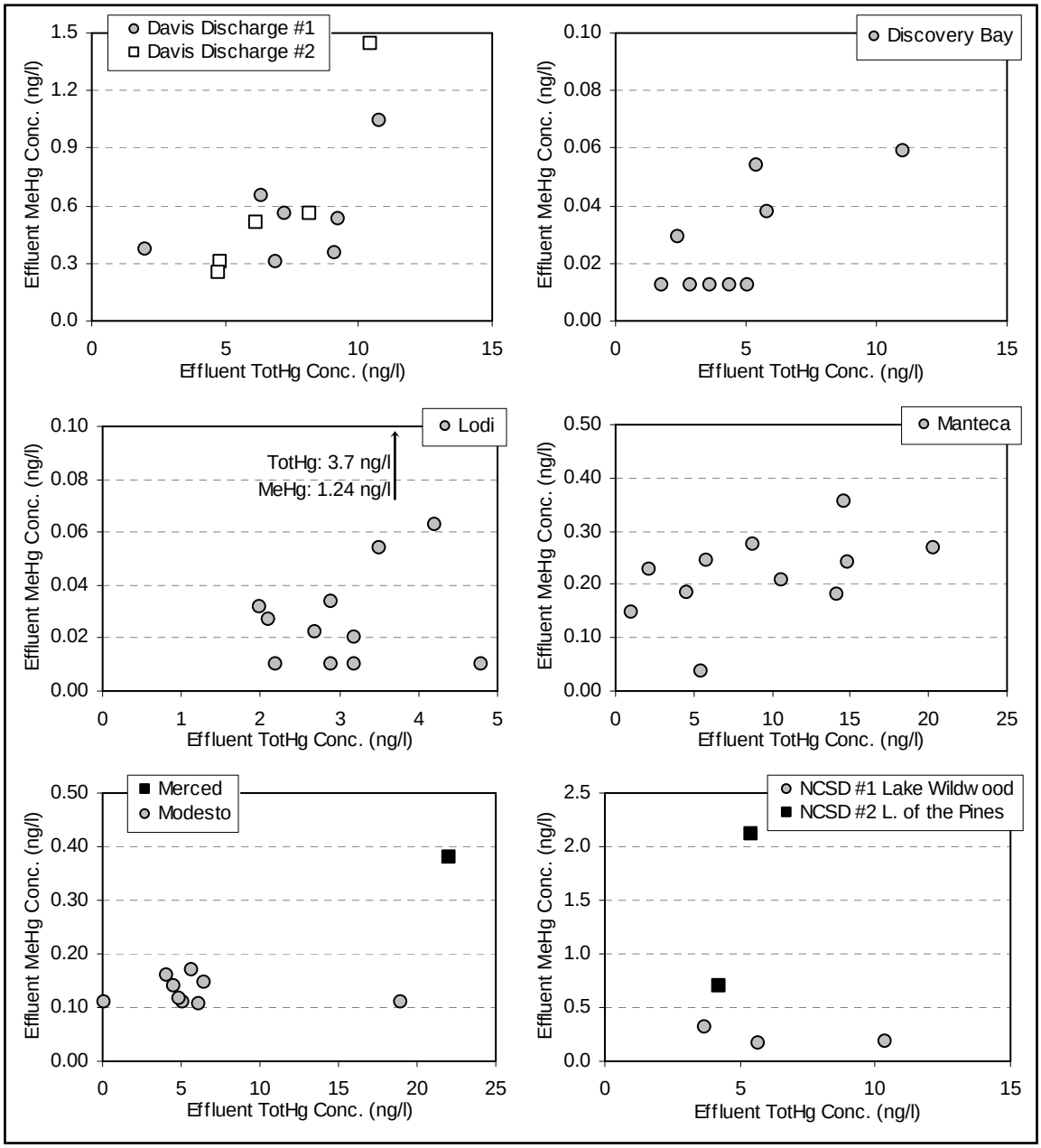

Figure 37a: Scatter-plots of Effluent Inorganic Mercury versus Effluent Methylmercury Concentrations for Each Municipal WWTP

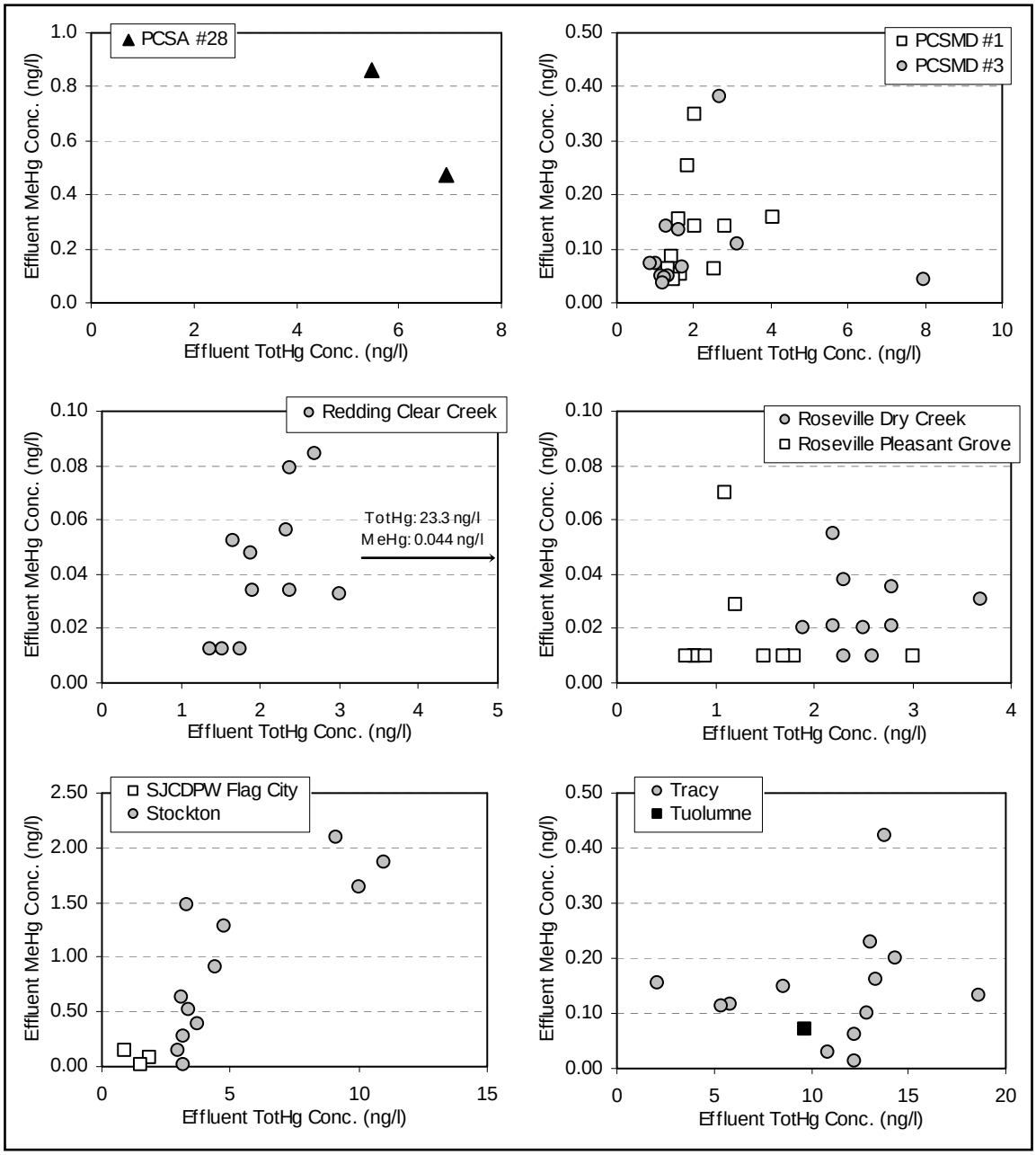

Figure 37b: Scatter-plots of Effluent Inorganic Mercury versus Effluent Methylmercury Concentrations for Each Municipal WWTP

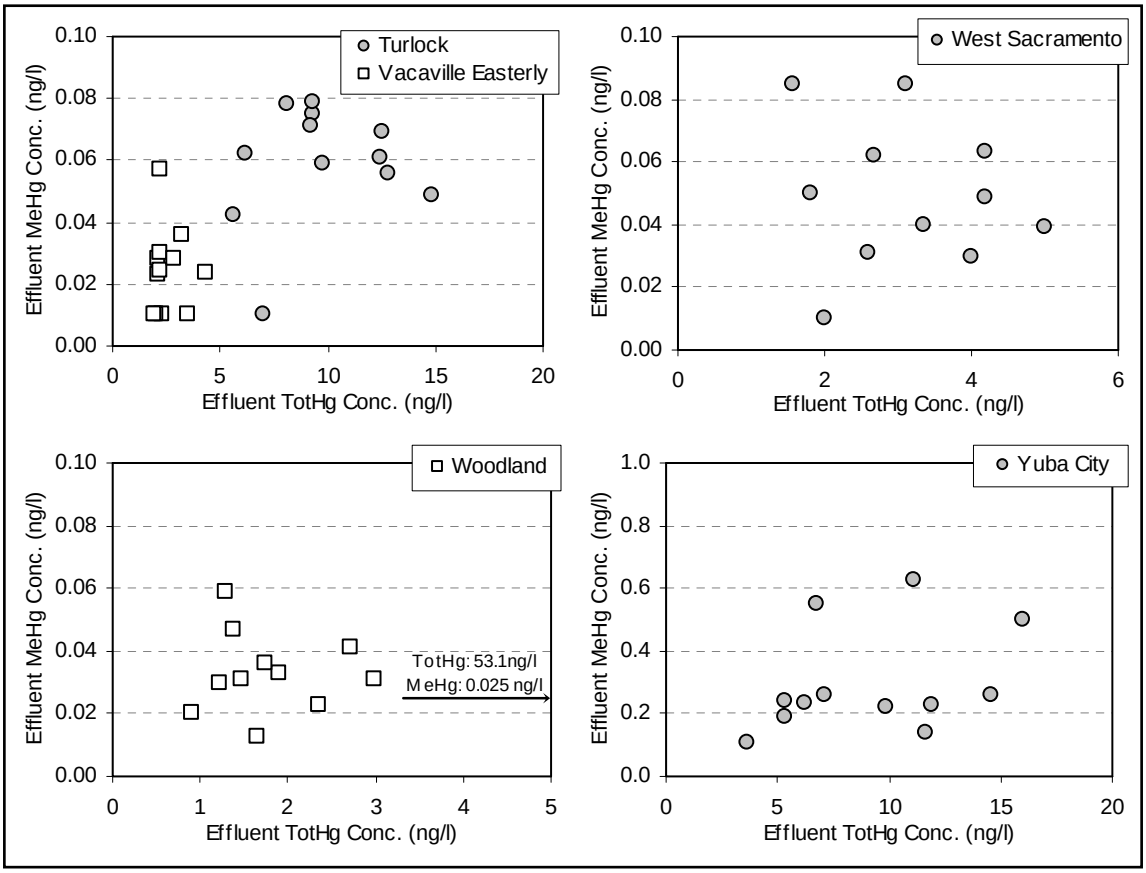

Figure 37c: Scatter-plots of Effluent Inorganic Mercury versus Effluent Methylmercury Concentrations for Each Municipal WWTP

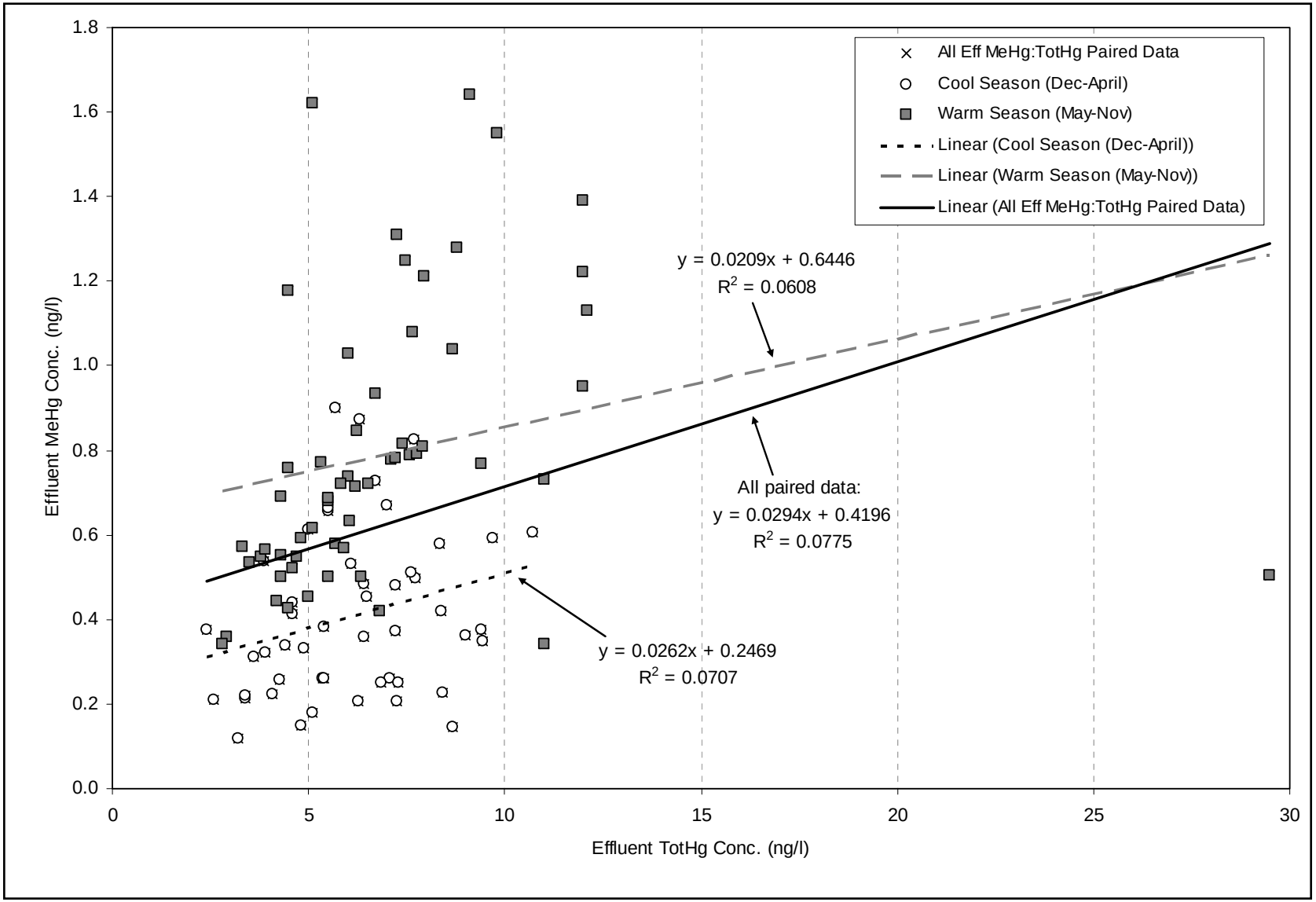

Figure 38: Scatter-plot of Effluent Inorganic Mercury versus Effluent Methylmercury Concentrations for the SRCSD Sacramento River WWTP

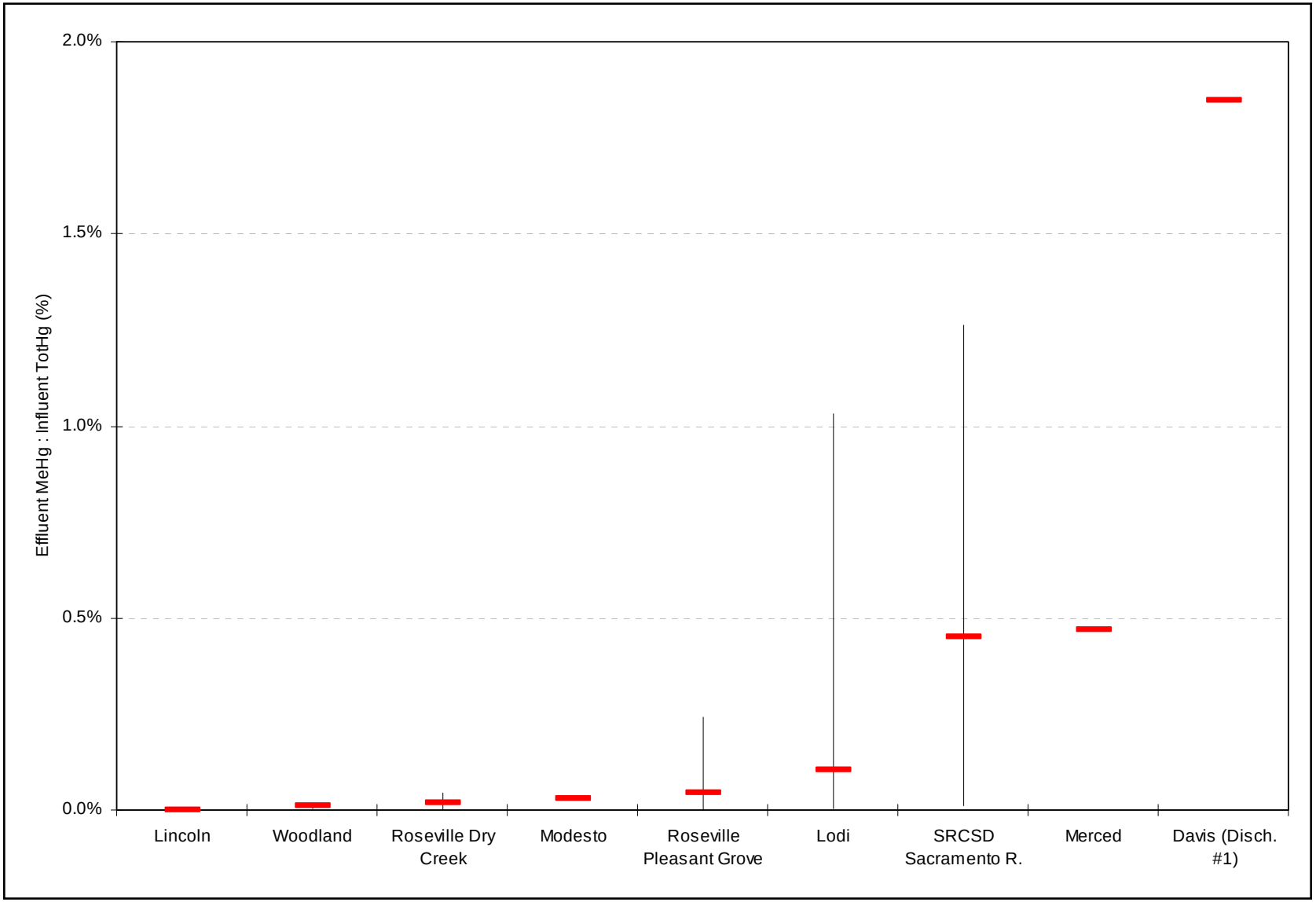

Figure 39: Average and Range of Effluent MeHg:Influent TotHg Concentration Ratios for Each Municipal WWTP

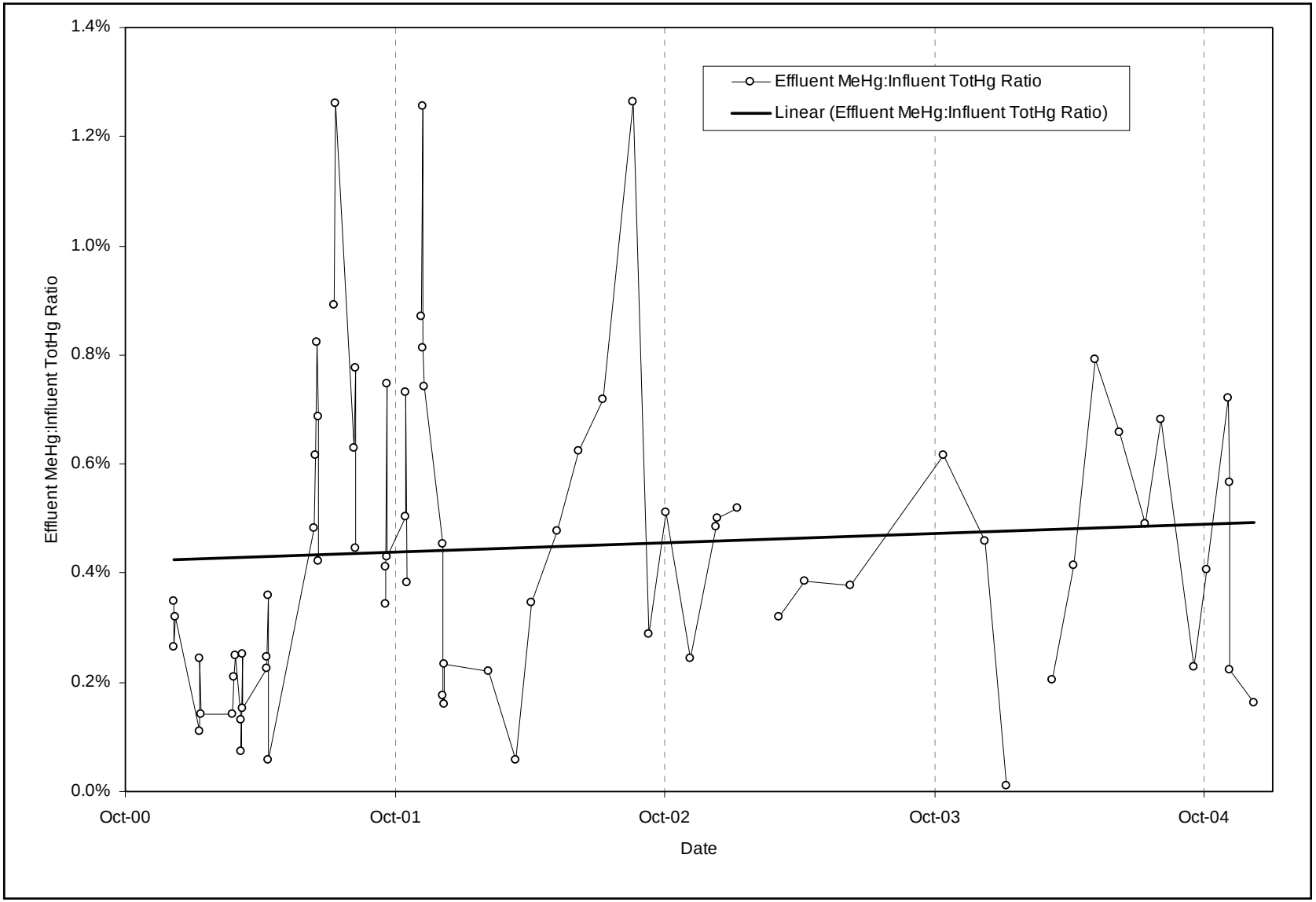

Figure 40: Time-series Graph of SRCSD Sacramento River WWTP Effluent MeHg:Influent TotHg Concentration Ratios

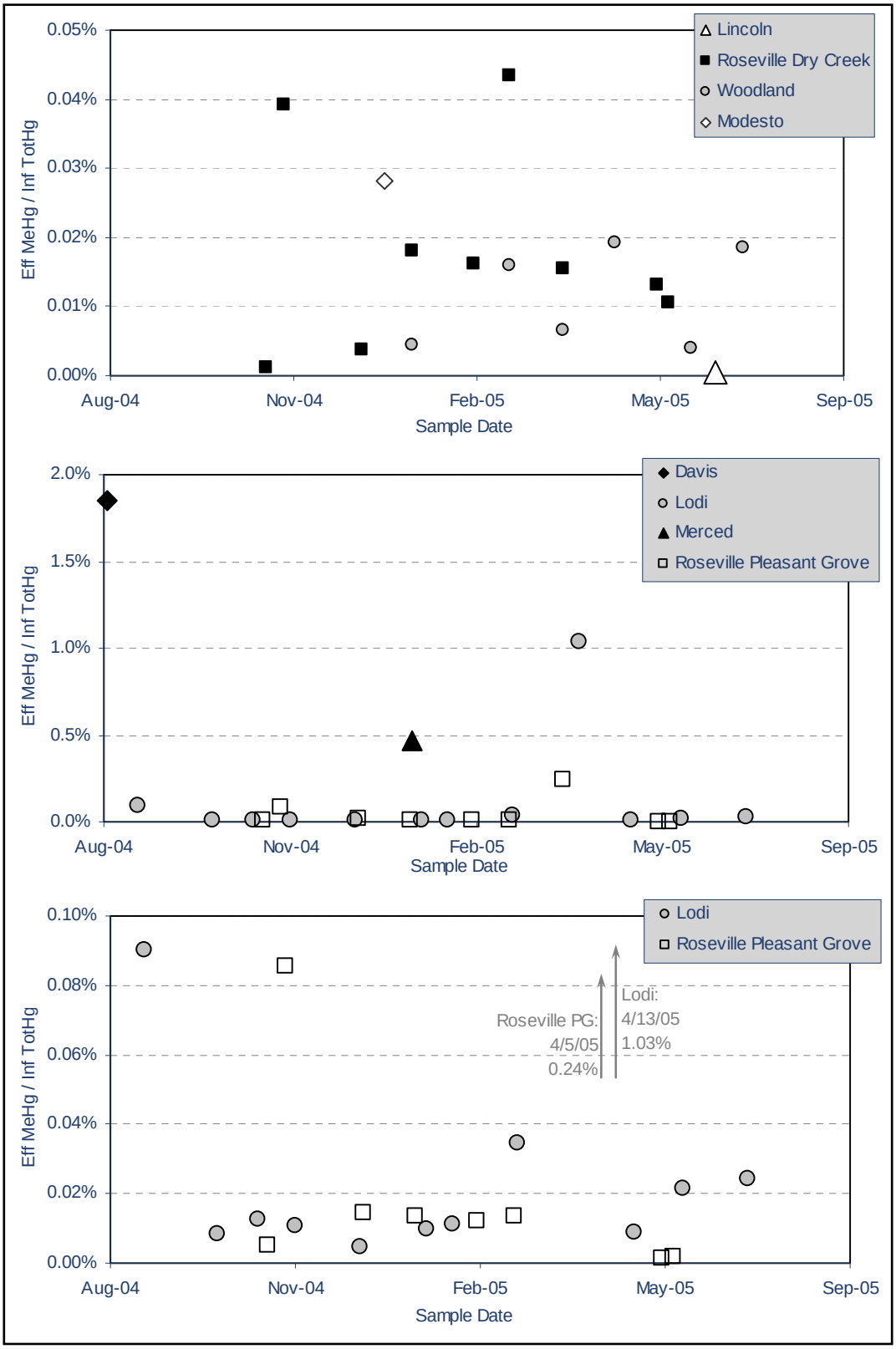

Figure 41: Time-series Graphs of Municipal WWTP Effluent MeHg:Influent TotHg Concentration Ratios

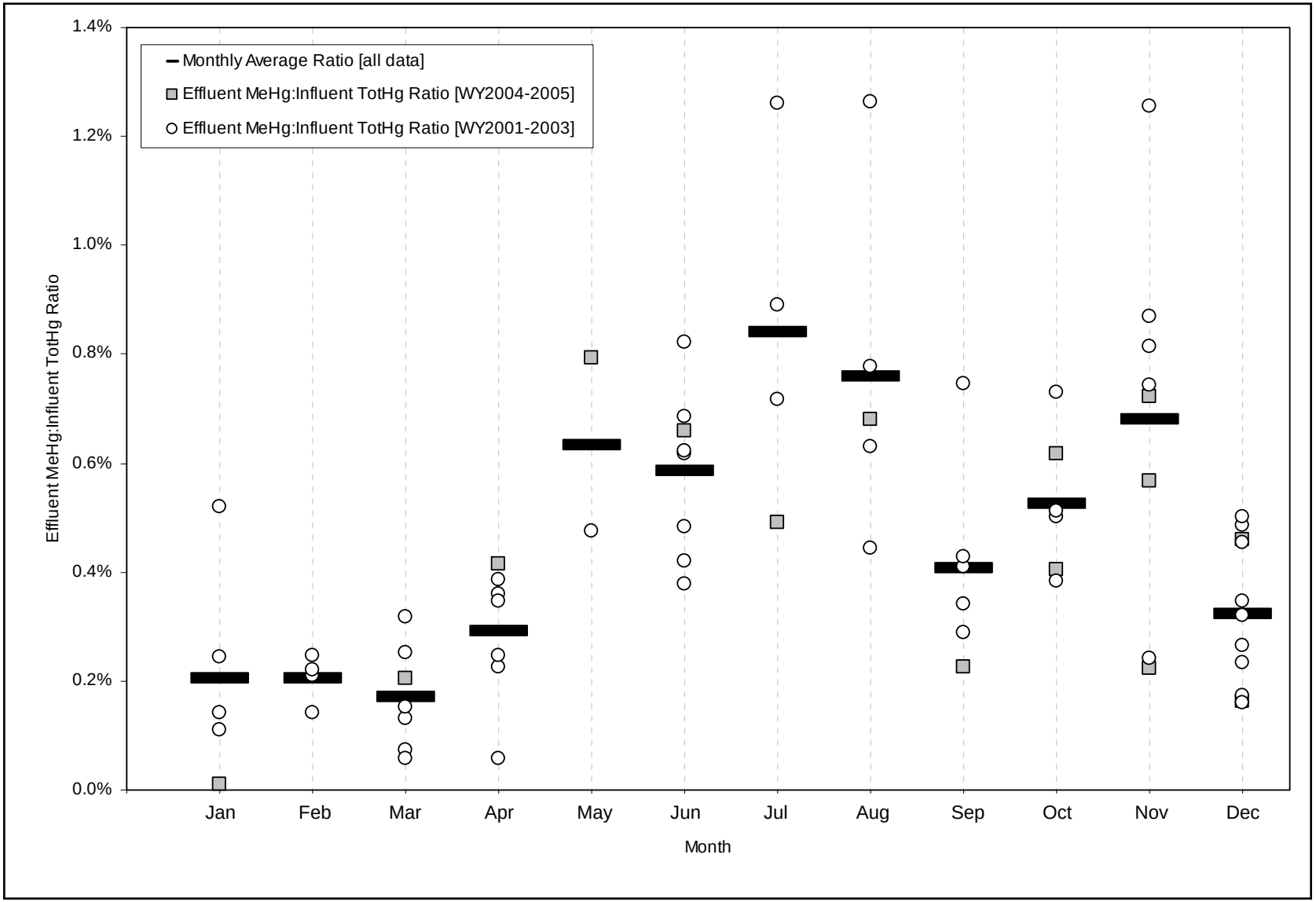

Figure 42: Monthly Effluent MeHg:Influent TotHg Concentration Ratios for the SRCSD Sacramento River WWTP from Dec. 2000 – Dec. 2004

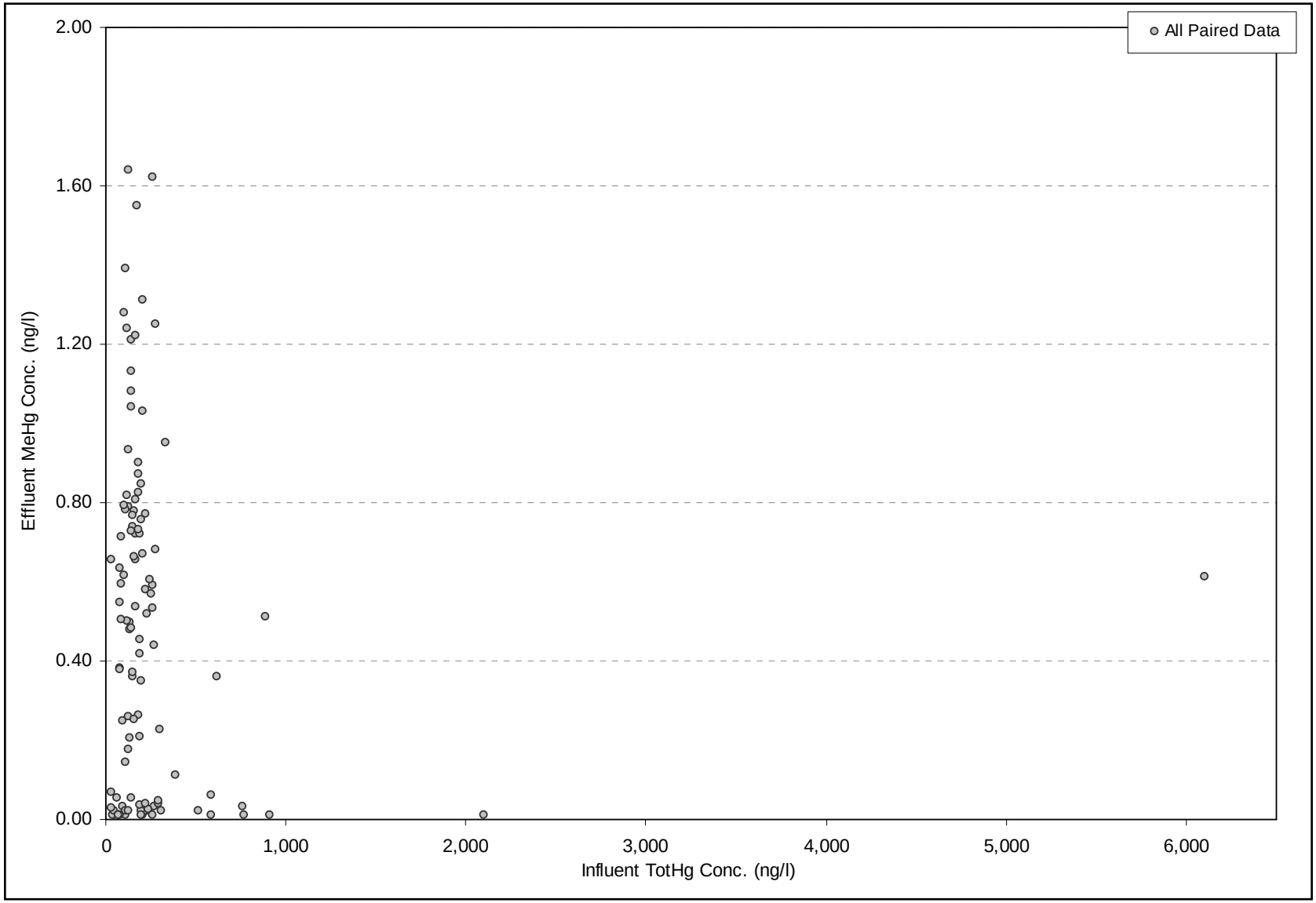

Figure 43a: Scatter-plot of Municipal WWTP Influent Inorganic Mercury versus Effluent Methylmercury Concentrations: All Paired Data [including SRCSD Sacramento WWTP data]

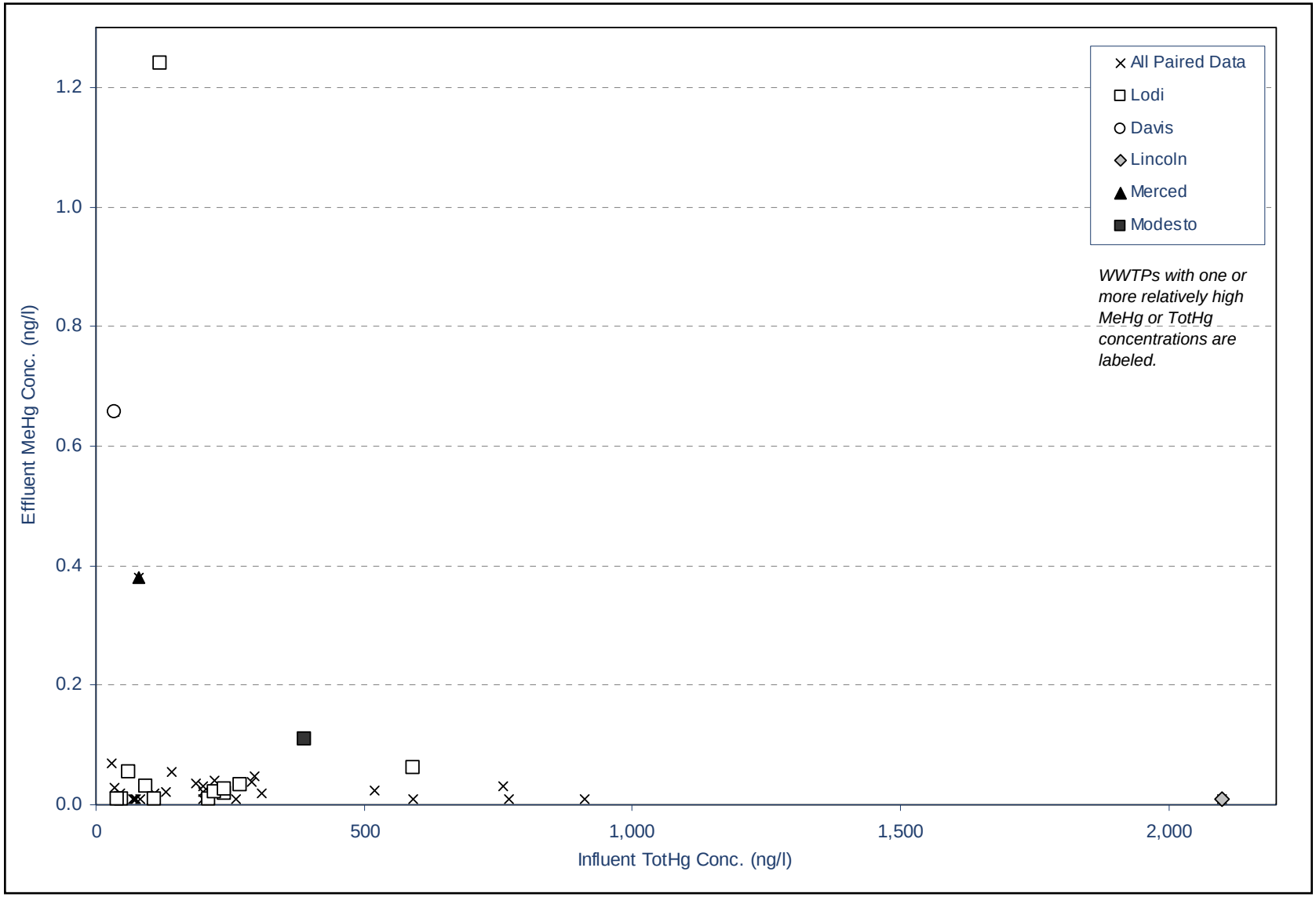

Figure 43b: Scatter-plot of Municipal WWTP Influent Inorganic Mercury versus Effluent Methylmercury Concentrations: All Paired Data [excluding SRCSD Sacramento WWTP data]

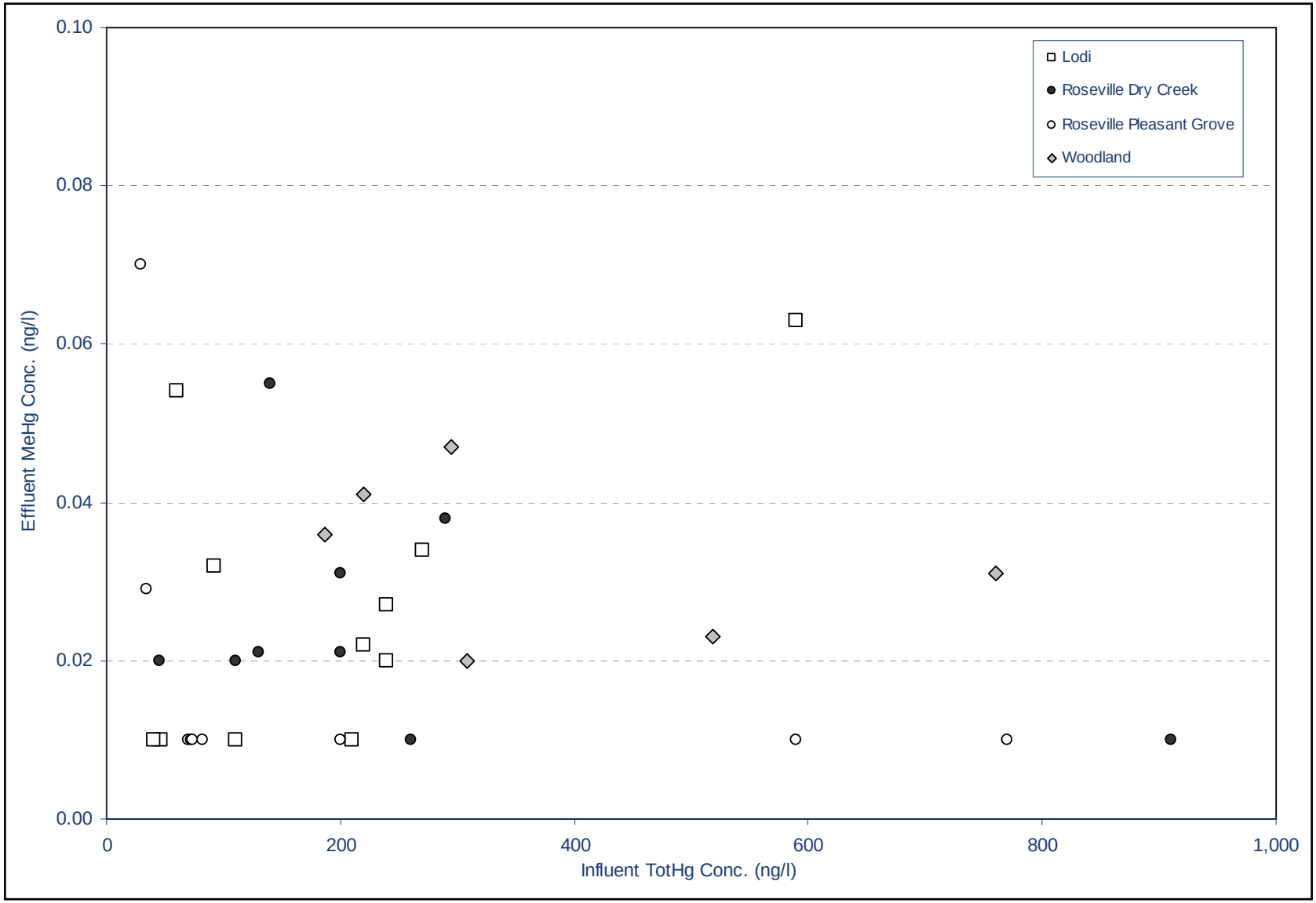

Figure 44: Scatter Plot of Municipal WWTP Influent Inorganic Mercury versus Effluent Methylmercury Concentrations: Zoomed to Show Typical Values

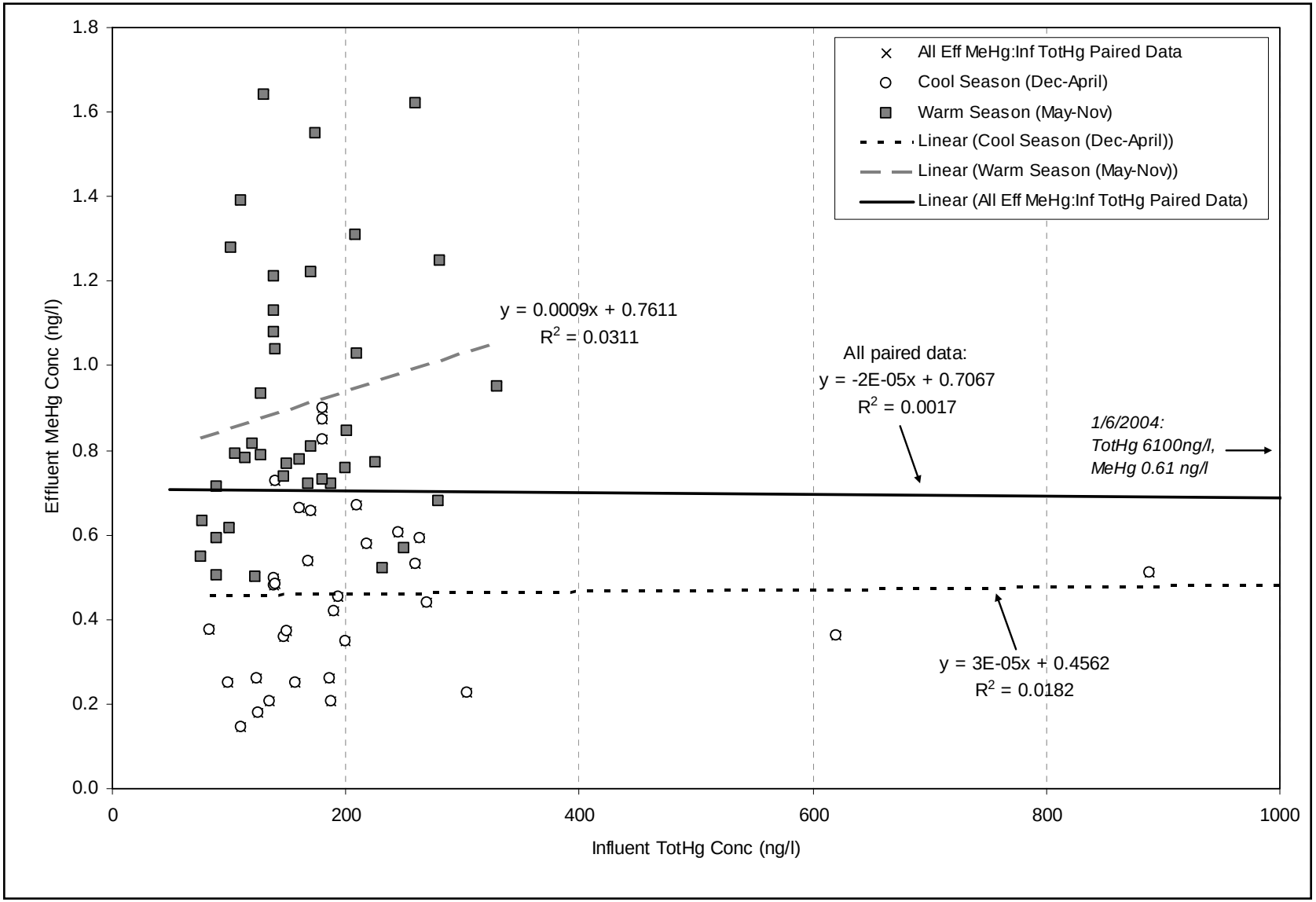

Figure 45a: Scatter-plot of Influent Inorganic Mercury versus Effluent Methylmercury Concentrations for the SRCSD Sacramento River WWTP

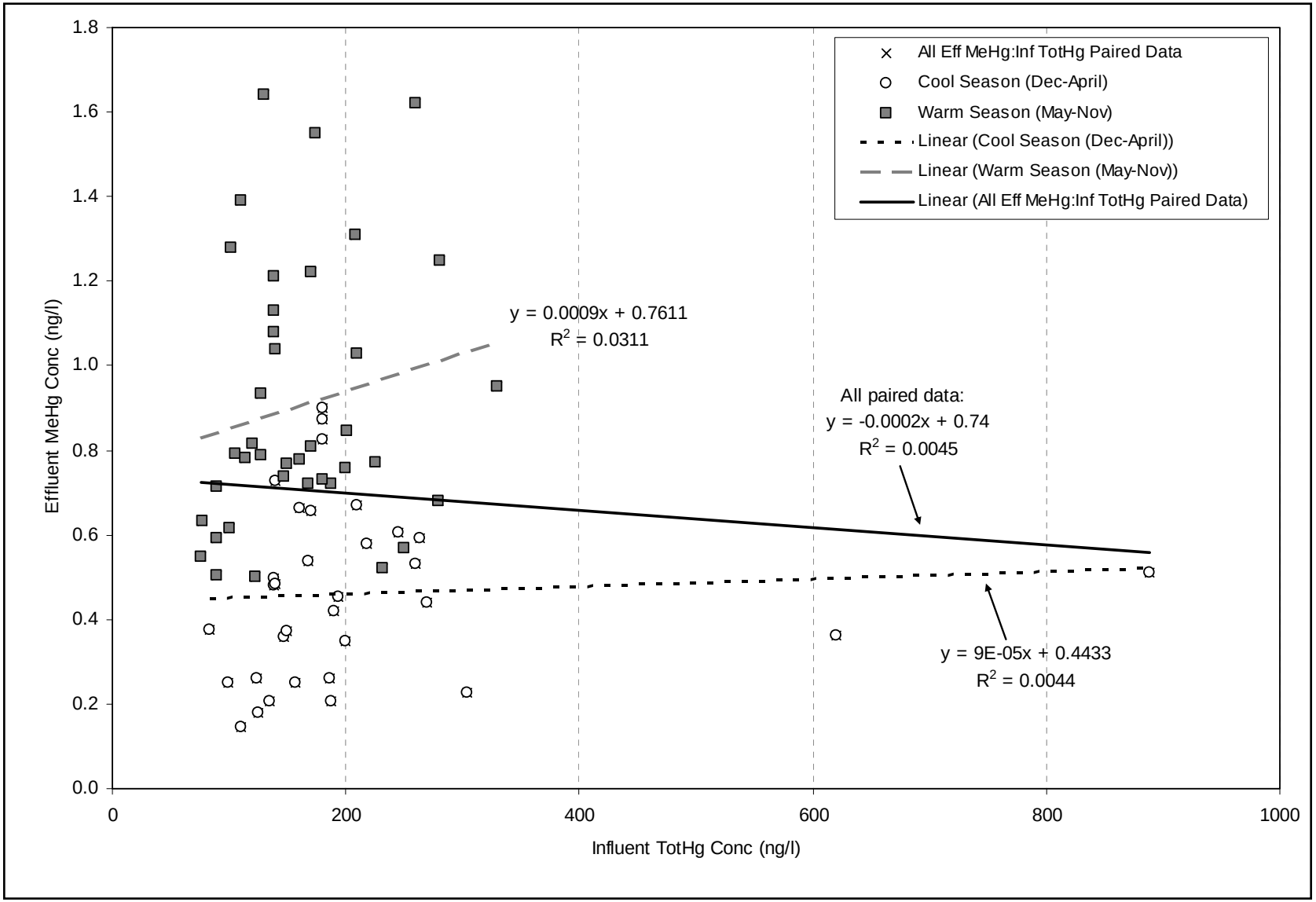

Figure 45b: Scatter-plot of Influent Inorganic Mercury versus Effluent Methylmercury Concentrations for the SRCSD Sacramento River WWTP (with the paired data that includes the anomalous value collected on 6 January 2004 removed)

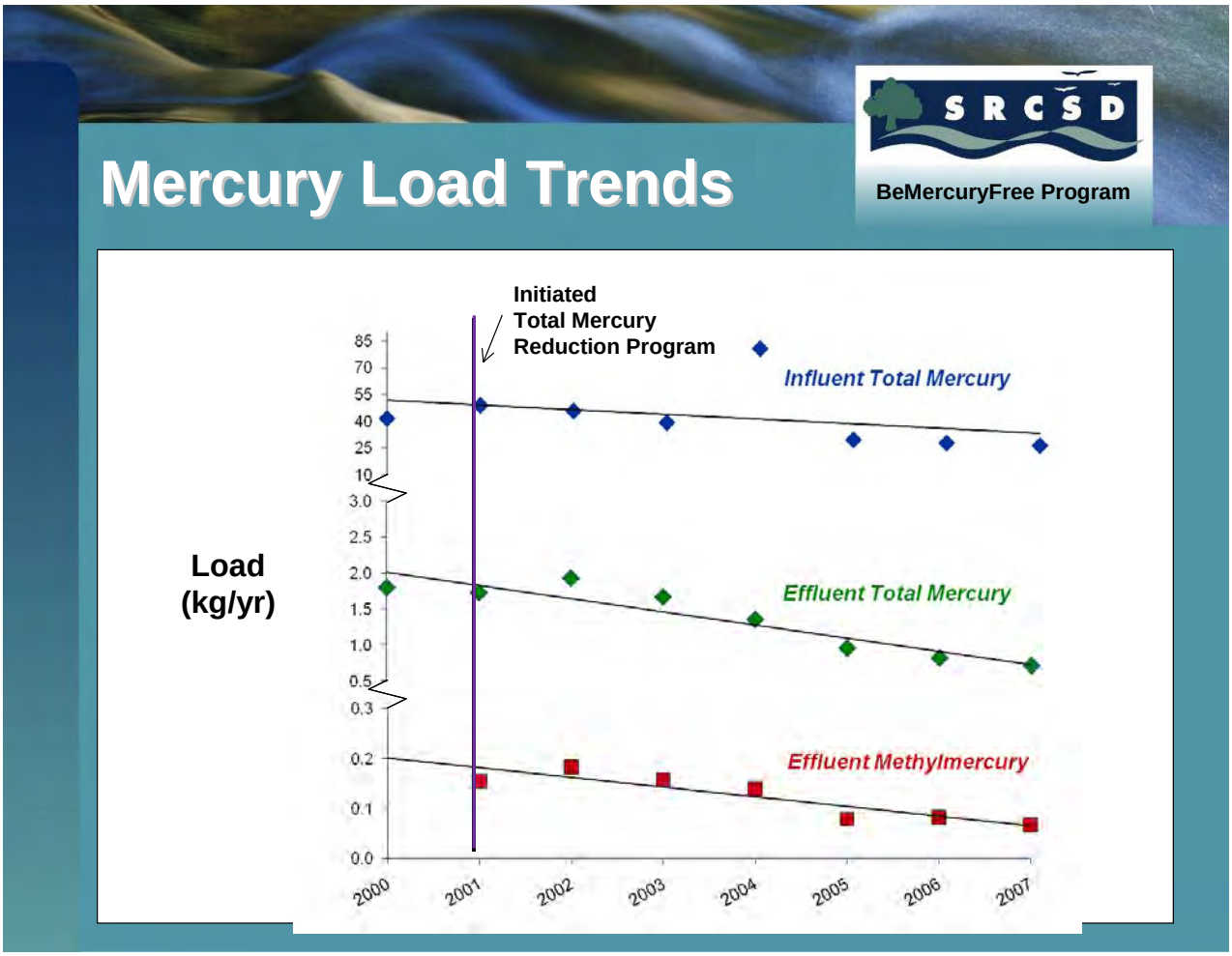

Figure 46: SRCSD Sacramento River WWTP Influent Inorganic Mercury and Effluent Inorganic Mercury and Methylmercury Loads

[Chart presented by the SRCSD District Engineer during testimony for the April 2008 Central Valley Water Board hearing for the Delta mercury control program.]

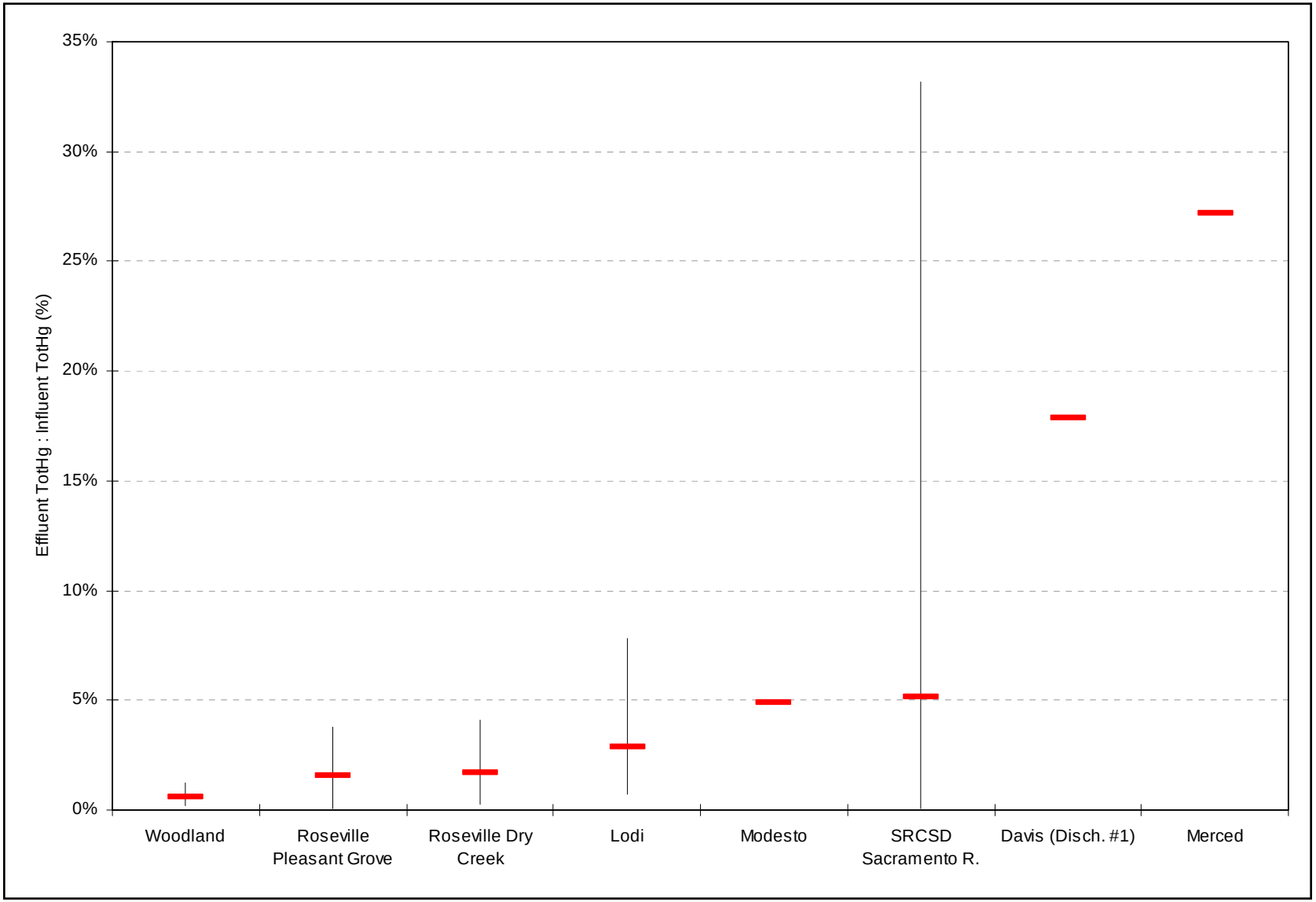

Figure 47: Average and Range of Effluent:Influent Inorganic Mercury Concentration Ratios for Each Municipal WWTP

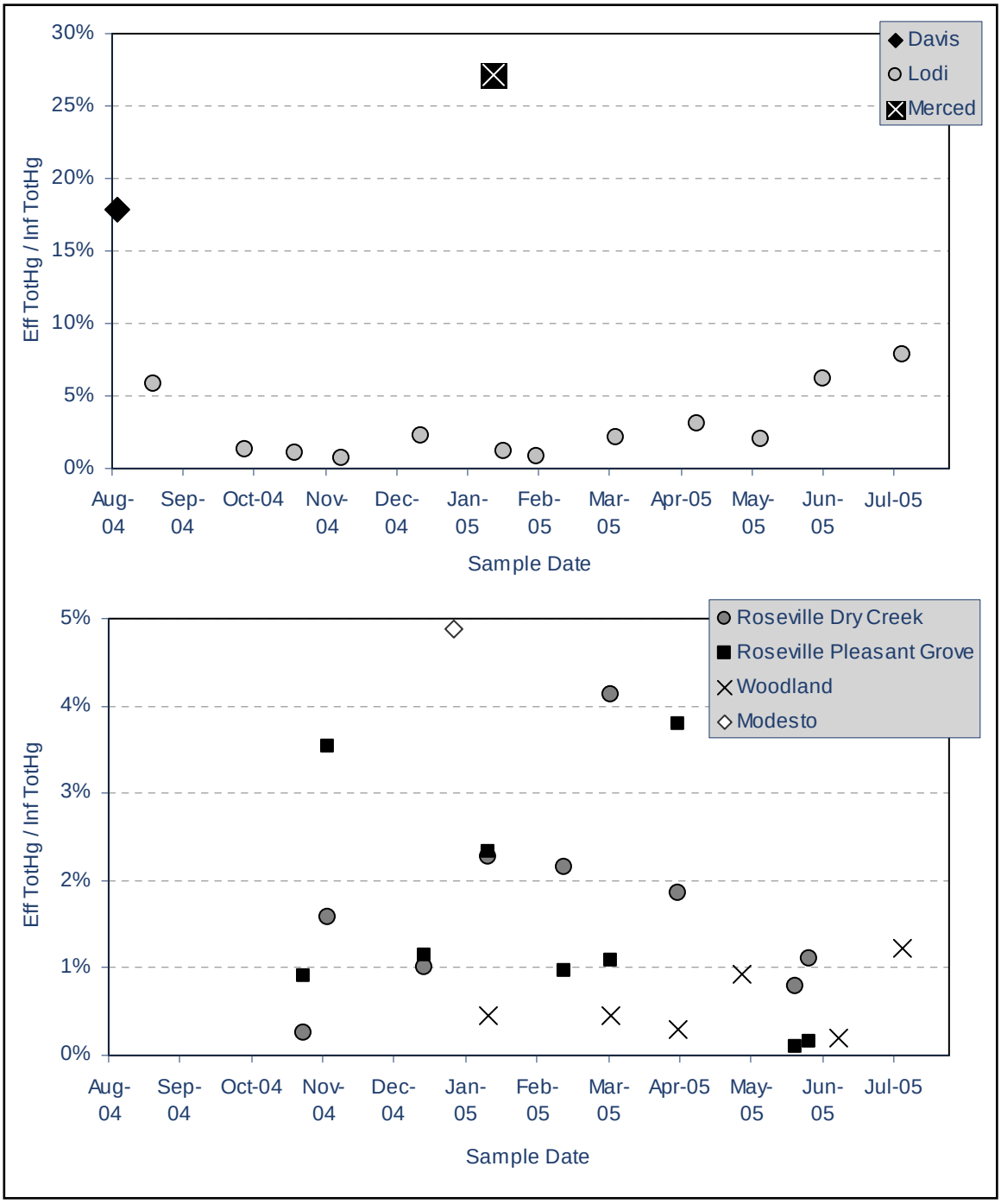

Figure 48: Time-series Graphs of Municipal WWTP Effluent:Influent Inorganic Mercury Concentration Ratios

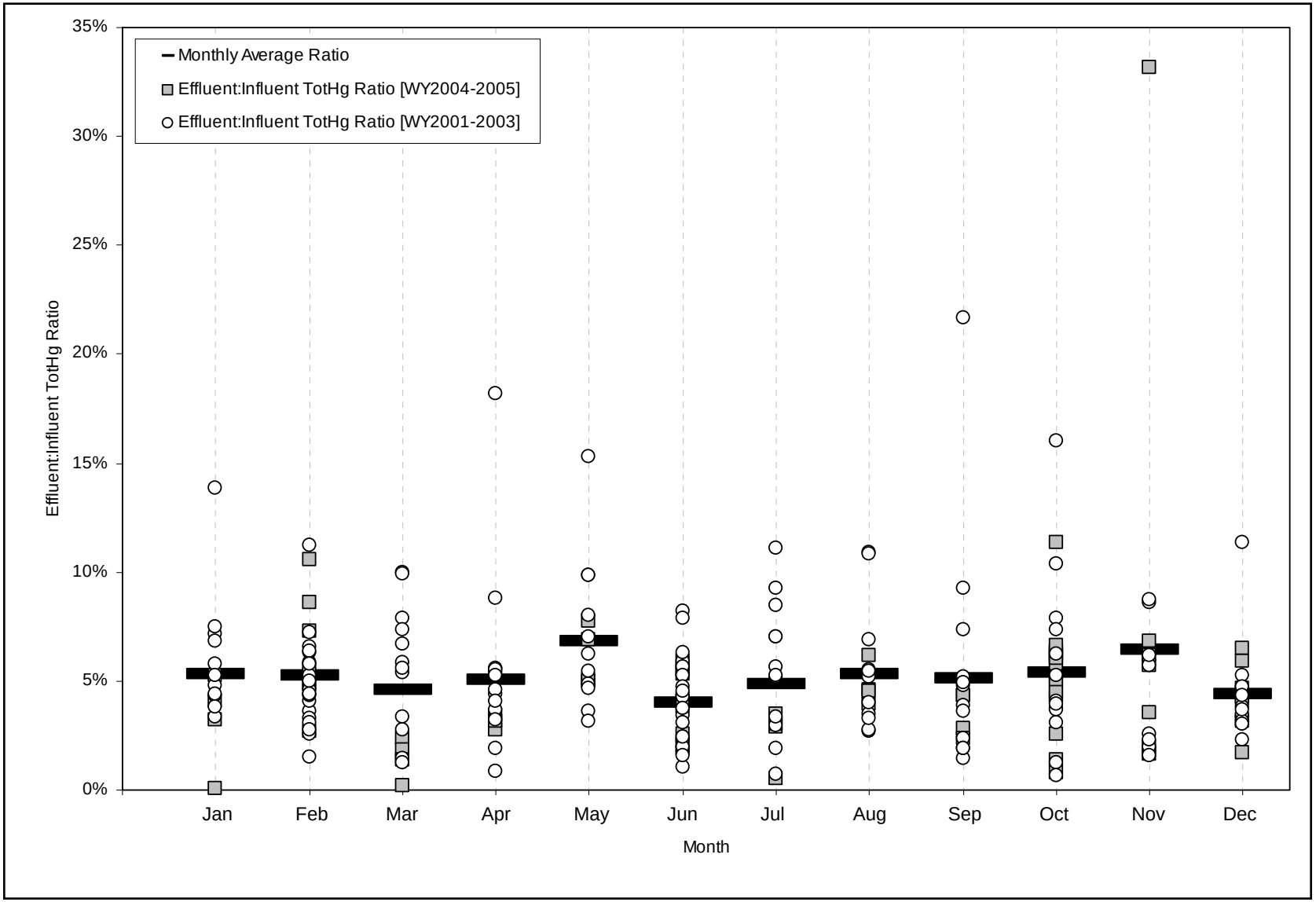

Figure 49: Monthly Effluent:Influent TotHg Concentration Ratios for the SRCSD Sacramento River WWTP from December 2000 – December 2004

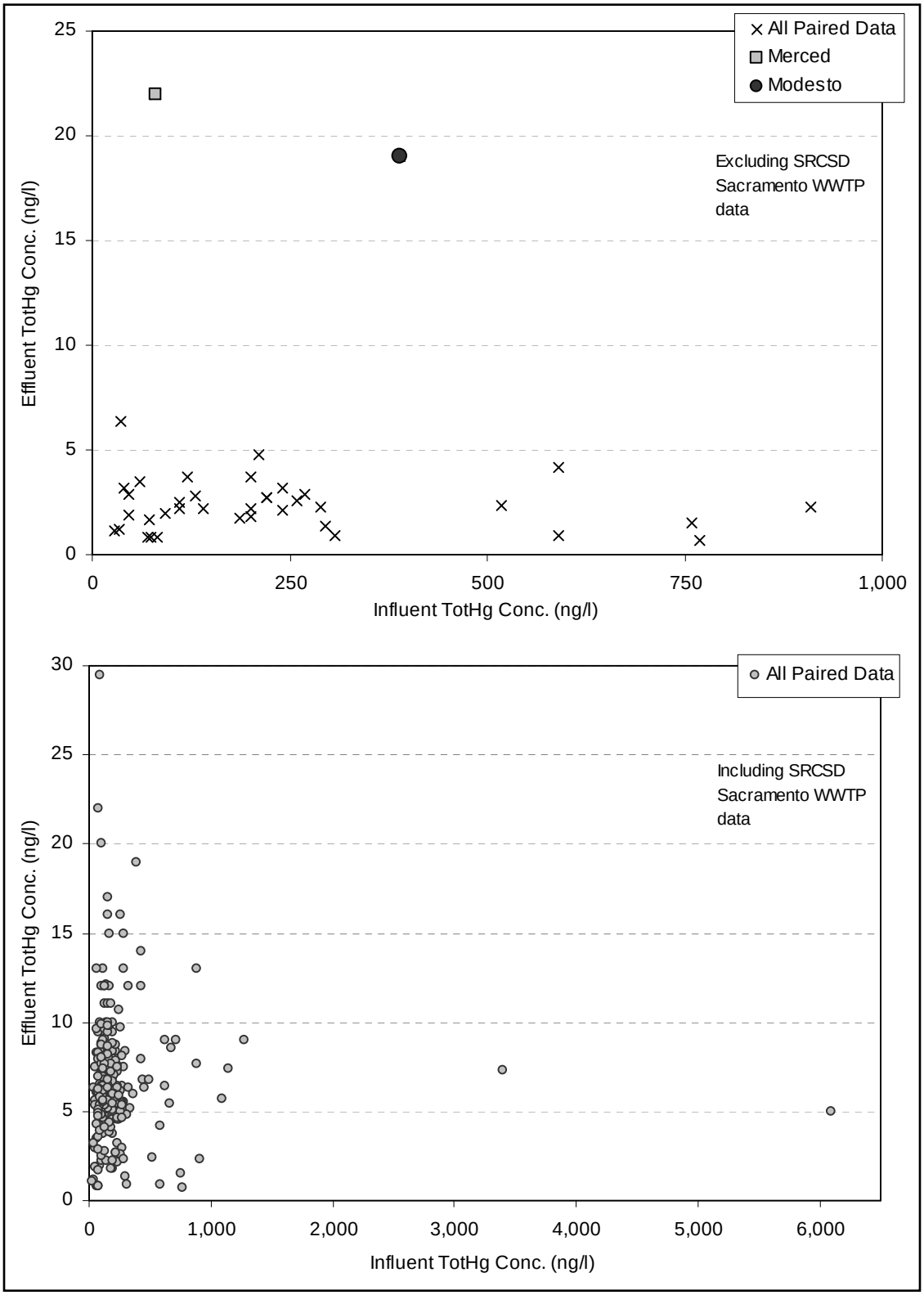

Figure 50: Scatter-plots of Municipal WWTP Influent Inorganic Mercury versus Effluent Inorganic Mercury Concentrations: All Paired Data

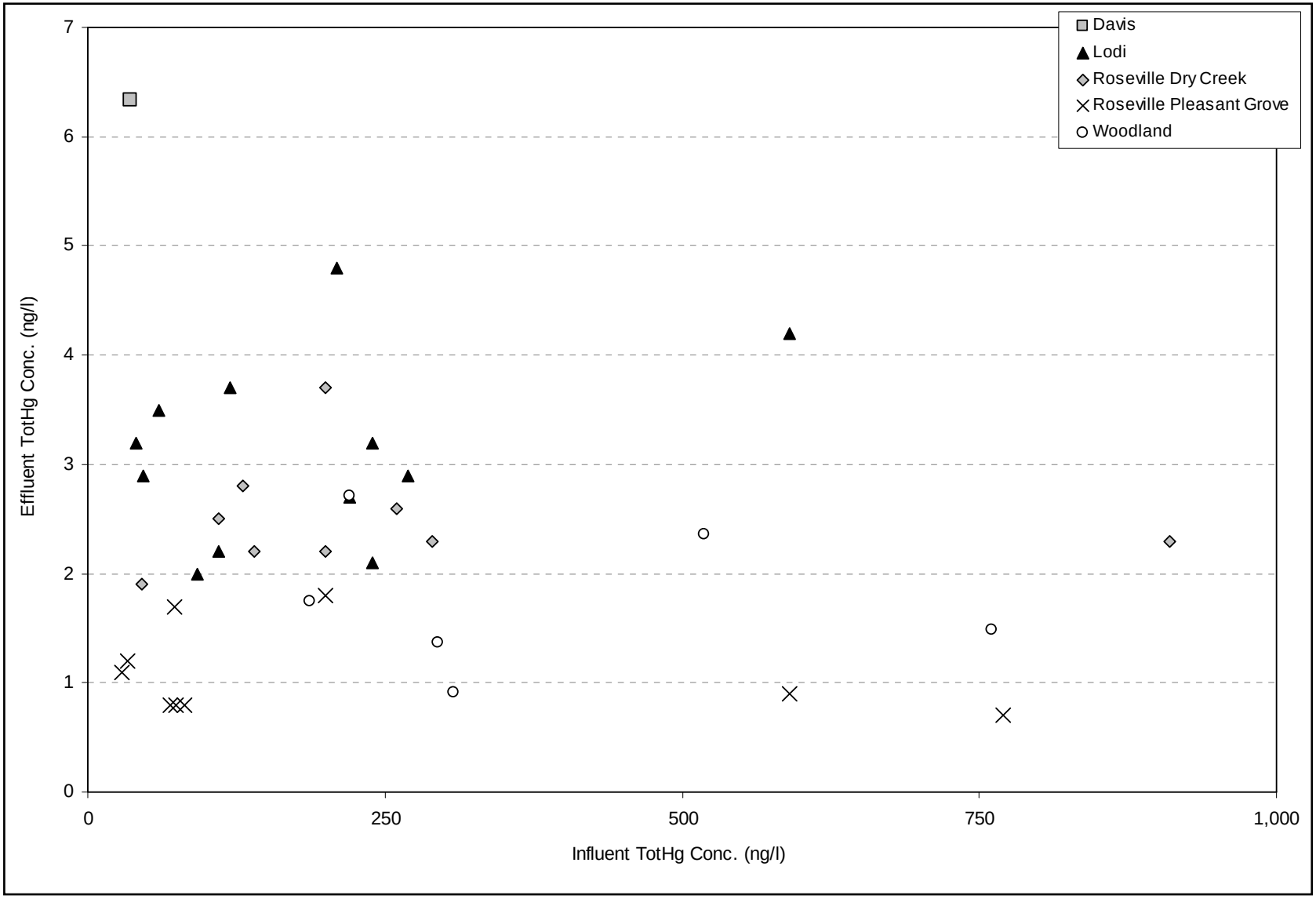

Figure 51: Scatter-plot of Municipal WWTP Influent Inorganic Mercury versus Effluent Inorganic Mercury Concentrations

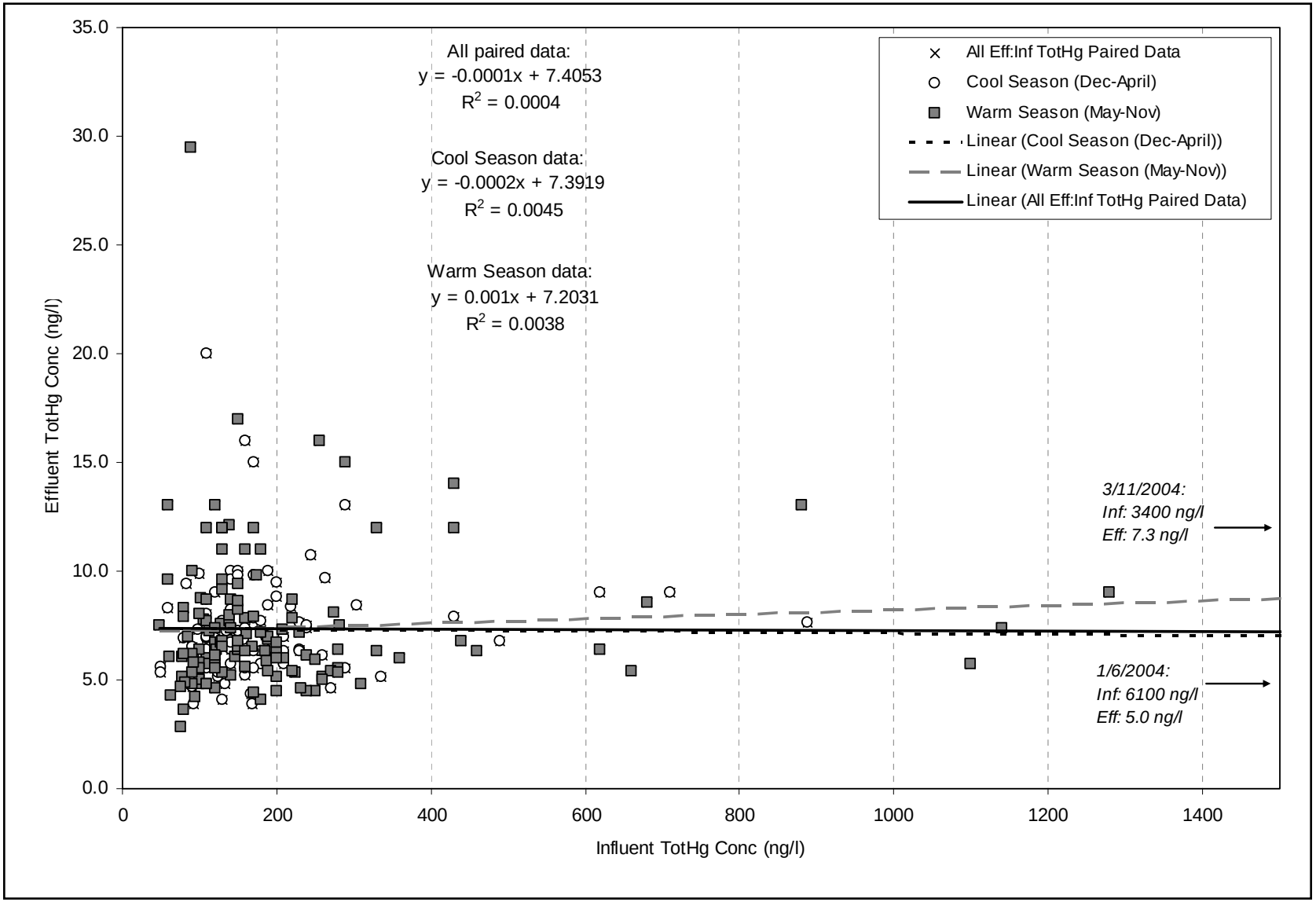

Figure 52: Scatter-plot of Influent Inorganic Mercury versus Effluent Inorganic Mercury Concentrations for the SRCSD Sacramento River WWTP

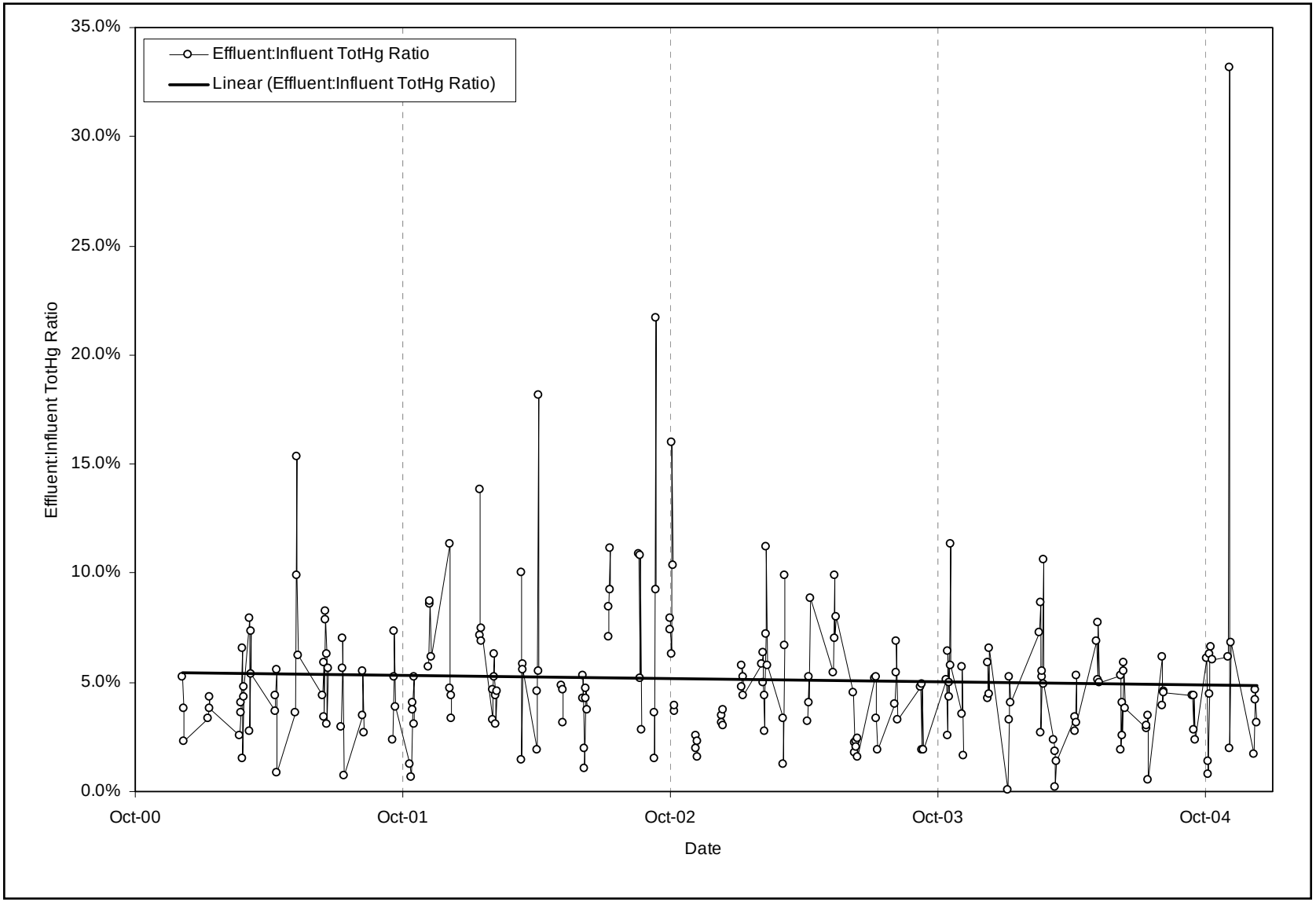

Figure 53: Time-series Graph of SRCSD Sacramento River WWTP Effluent:Influent Inorganic Mercury Concentration Ratios

APPENDIX A
EXAMPLE OF CALIFORNIA WATER CODE SECTION 13267 ORDER LETTER FOR EFFLUENT METHYLMERCURY MONITORING (4 PAGES) & DISCHARGERS TO WHICH A LETTER WAS SENT

California Regional Water Quality Control Board

Central Valley Region

Robert Schneider, Chair

Terry Tamminen
Secretary for
Environmental
Protection

Sacramento Main Office
Internet Address: http://www.swrcb.ca.gov/rwqcb5
11020 Sun Center Drive #200 Rancho Cordova, CA 95670-6114
Phone (916) 464-3291

Arnold Schwarzenegger
Governor

16 June 2004

CERTIFIED MAIL
«Certified_Mail» «Cert_2»

«MAIL_CONTACT»
«MAIL_NAME»
«MAIL_STREET»
«MAIL_CITY», «MAIL_STATE» «MAIL_ZIP»

ORDER FOR UNFILTERED METHYLMERCURY WASTE DISCHARGE DATA PURSUANT TO CALIFORNIA WATER CODE SECTION 13267 (*MONTHLY* SAMPLING) NPDES NO. «NPDES_NO»

Section 303(d) of the federal Clean Water Act requires States to list water bodies that do not meet water quality objectives to protect their beneficial uses and to develop and implement Total Maximum Daily Load (TMDL) control programs to eliminate the impairment of beneficial uses.

The Sacramento and San Joaquin Rivers and associated Delta Estuary were placed on the 303(d) list because of elevated methylmercury concentrations in fish. Recent data demonstrate a statistically significant correlation between methylmercury concentrations in water and fish, i.e., as concentrations of methylmercury increase in the water column, concentrations of methylmercury also increase in fish resident in that water column. The data thus suggest that the annual median methylmercury concentration of a water body is a major factor determining resident fish tissue methylmercury levels. The proposed TMDL goal to protect Delta beneficial uses is 0.05 nanograms per liter (ng/l) methylmercury in water.

Limited methylmercury effluent data are available for local NPDES facilities. A recent survey by the Regional Board found considerable variability between facilities and demonstrated that some plants were discharging methylmercury above the proposed TMDL goal. Table 1 summarizes data collected by the Regional Board in February and March of 2004 as well as data collected by the Sacramento Regional County Sanitation District from a year-long study in 2001.

Section 13267 of the California Water Code states in part that a regional board may investigate the quality of waters within its region, and in doing so may require dischargers to furnish technical or monitoring reports which the regional board requires. The burden, including costs, of these reports must bear a reasonable relationship to the need for the report and the benefits to be obtained from the reports.

The monitoring reports required by this letter are necessary to determine the extent to which NPDES facilities are contributing methylmercury in concentrations that impair beneficial uses of receiving waters. Preliminary load calculations using the information shown in Table 1 estimate that POTWs discharge significant portions of the total methylmercury loading to the Delta. Accurate discharge information will be required from treatment facilities to complete the TMDL.

Table 1. Summary of unfiltered methylmercury concentrations in effluent from POTW's located in the Central Valley of California.

Facility	# of Sampling Events	Mean Concentration (ng/l)	Range (ng/l)
Sacramento Regional County Sanitation District	45	0.73	0.14-2.93
Stockton STP	2	0.34	0.13-0.59
Vacaville Easterly STP	2	0.10	0.09-0.11
West Sacramento STP	2	0.04	0.03-0.05
City of Roseville	2	0.01	0.01-0.01

Therefore pursuant to Section 13267 of the California Water Code, you are required to submit effluent methylmercury monitoring data for your facility. In most cases, this monitoring will be in addition to monitoring required in your NPDES Permit.

Instantaneous grab samples shall be collected monthly for one year (August 2004-July 2005) from the facility's effluent. Intermittent or seasonal dischargers shall collect monthly samples during those months for which a discharge occurs. The samples must be collected downstream from the last connection through which wastes can be admitted into the outfall, and shall be representative of the quality of the discharge from the treatment plant. Unfiltered methylmercury samples shall be taken using clean hands/dirty hands procedures[1] and shall be analyzed by U.S. EPA method 1630/1631 (Revision E) with a method detection limit of 0.02 ng/l. A matrix spike/matrix spike duplicate shall also be analyzed with either the first or second set of samples to insure an acceptable methylmercury recovery rate in your effluent. A travel-blank must also be collected and analyzed with every other set of samples. Any other methylmercury monitoring data collected by your plant during the above period shall also be reported to the Regional Board. If your facility is currently collecting total mercury data, methylmercury samples should be collected concurrently. A partial list of laboratories performing U.S. EPA method 1630/1631 is attached as Table 2.

While not required by this letter, we are also recommending that instantaneous grab samples be collected from the facility's upstream receiving water and the main influent to determine the methylmercury treatment efficiency of your facility.

Please submit quarterly reports summarizing the monitoring results to the Regional Board. The reports are due by 31 October 2004, 31 January 2005, 30 April 2005, and 31 July 2005. Your cooperation with this special discharge monitoring requirement is sincerely appreciated. However, we must advise that failure or refusal to comply with this request as required by Section 13267 of the California Water Code or falsifying any information provided may be subject to an administrative civil liability of up to $1,000 per day of violation in accordance with Section 13268.

[1] Described in U.S. EPA method 1669: Sampling Ambient Water for Trace Metals at EPA Water Quality Criteria Levels for collection of equipment blanks (section 9.4.4.2)

Please contact your regular Regional Board staff representative if you have any questions regarding this order.

THOMAS R. PINKOS
Executive Officer

Attachment

Table 2. List of Analytical Laboratories Measuring Methylmercury by U.S. EPA Method 1630/1631

Presence on the list does not constitute endorsement by the Regional Board.

Facility	Contact	Phone
Battelle Marine Science Laboratory 1529 West Sequim Bay Road Sequim, WA 98382	Brenda Lasorsa	360-681-3650
Frontier GeoSciences 414 Pontius Ave N Seattle WA 98109 http://www.frontiergeosciences.com	Michelle Gauthier	206-622-6960
Brook-Rand Trace Metal Analysis and Products 3958 6th Ave N.W. Seattle WA 98107 http://www.brooksrand.com	Colin Davis	206-632-6206

Table A.1: NPDES-Permitted Facilities Required to Conduct Effluent Methylmercury Monitoring under California Water Code Section 13267.

AGENCY NAME	FACILITY NAME	NPDES NO	MONITORING FREQUENCY [a]
AEROJET GENERAL CORPORATION	INTERIM GROUNDWATER WTP	CA0083861	B
AEROJET GENERAL CORPORATION	SACRAMENTO FACILITY	CA0004111	B
AFB CONVERSION AGENCY	A C & W - GROUNDWATER TREATMENT	CA0083992	Q
ANDERSON, CITY OF	ANDERSON WWTP	CA0077704	M
ATWATER, CITY OF	ATWATER WWTP	CA0079197	M
AUBURN, CITY OF	AUBURN WWTP	CA0077712	M
BELL CARTER OLIVE COMPANY INC	BELL CARTER INDUSTRIAL WWTP	CA0083721	Q
BELL CARTER OLIVE COMPANY INC	PLANT 1	CA0081639	B
BELLA VISTA WD	BELLA VISTA WTP	CA0080799	B
BIGGS, CITY OF	BIGGS WWTP	CA0078930	Q
BRENTWOOD, CITY OF	BRENTWOOD WWTP	CA0082660	M
BROWN SAND, INC.	MANTECA AGGREGATE SAND PLANT [b]	CA0082783	Q
CA DEPT OF FISH & GAME	DARRAH SPRINGS HATCHERY	CA0004561	Q
CA DEPT OF FISH & GAME	FEATHER RIVER HATCHERY	CA0004570	Q
CA DEPT OF FISH & GAME	MERCED RIVER FISH HATCHERY	CA0080055	Q
CA DEPT OF FISH & GAME	MOCCASIN FISH HATCHERY	CA0004804	Q
CA DEPT OF FISH & GAME	MOKELUMNE RIVER FISH HATCHERY	CA0004791	Q
CA DEPT OF FISH & GAME	NIMBUS HATCHERY	CA0004774	Q
CA DEPT OF FISH & GAME	SAN JOAQUIN FISH HATCHERY	CA0004812	Q
CA DEPT OF FISH & GAME	THERMALITO ANNEX HATCHERY	CA0082350	Q
CA DEPT OF GENERAL SERVICES	STATE PRINTING & WAREHOUSES	CA0078875	Q
CA (STATE OF) CENTRAL PLANT	CENTRAL HEATING/COOLING FAC	CA0078581	Q
CALAVERAS TROUT FARM, INC	TROUT REARING FACILITY	CA0081752	Q
CALIF AMMONIA COMPANY	CALAMCO - STOCKTON TERMINAL	CA0083968	Q
CALIFORNIA DAIRIES, INC	LOS BANOS FOODS, INC	CA0082082	Q
CALPINE CORPORATION	GREENLEAF UNIT ONE COGEN PLANT	CA0081566	Q
CANADA COVE L.P.	FRENCH CAMP GOLF & RV PARK WWTP	CA0083682	Q
CHICO, CITY OF	CHICO REGIONAL WWTP	CA0079081	M
CLEAR CREEK CSD	CLEAR CREEK WTP	CA0083828	B
COLFAX, CITY OF	COLFAX WWTP	CA0079529	Q
COLUSA, CITY OF	COLUSA WWTP	CA0078999	Q
CORNING, CITY OF	CORNING INDUST/DOMESTIC WWTP	CA0004995	Q
CRYSTAL CREEK AGGREGATE INC	CRYSTAL CREEK AGGREGATE	CA0082767	B
DAVIS, CITY OF	CITY OF DAVIS WWTP	CA0079049	M
DEFENSE LOGISTICS AGENCY, ASCW	DDJC, SHARPE - GW CLEANUP	CA0081931	Q
DEUEL VOCATIONAL INSTITUTE	DEUEL VOCATNL INST. WWTP	CA0078093	Q
DISCOVERY BAY CSD	DISCOVERY BAY WWTP	CA0078590	M
DONNER SUMMIT PUBLIC UTILITY	DONNER SUMMIT WWTP	CA0081621	Q
EAST BAY MUD	CAMANCHE DAM POWER HOUSE	CA0082040	Q

Table A.1: NPDES-Permitted Facilities Required to Conduct Effluent Methylmercury Monitoring under California Water Code Section 13267.

AGENCY NAME	FACILITY NAME	NPDES NO	MONITORING FREQUENCY [(a)]
EL DORADO ID	DEER CREEK WWTP	CA0078662	M
EL DORADO ID	EL DORADO HILLS WWTP	CA0078671	M
FORMICA CORPORATION	SIERRA PLANT	CA0004057	Q
GALT, CITY OF	GALT SD WWTP	CA0081434	M
GAYLORD CONTAINER CORPORATION	ANTIOCH PULP & PAPER MILL	CA0004847	M
GENERAL ELECTRIC CO	GWCS	CA0081833	Q
GRASS VALLEY, CITY OF	GRASS VALLEY WWTP	CA0079898	M
GWF POWER SYSTEMS, INC.	GWF POWER SYSTEMS, SITE IV	CA0082309	Q
HERSHEY FOODS CORP	HERSHEY CHOCOLATE USA, OAKDALE	CA0004146	Q
JACKSON, CITY OF	CITY OF JACKSON WWTP	CA0079391	Q
LEHIGH SOUTHWEST CEMENT CO	LEHIGH SOUTHWEST CEMENT CO	CA0081191	B
LINCOLN, CITY OF	CITY OF LINCOLN WWTP	CA0084476	M
LINDA CO WATER DISTRICT	LINDA CO WTR DIST WWTP	CA0079651	Q
LIVE OAK, CITY OF	CITY OF LIVE OAK WWTP	CA0079022	Q
LODI, CITY OF	WHITE SLOUGH WWTP	CA0079243	M
MANTECA, CITY OF	MANTECA WWTP	CA0081558	M
MARIPOSA PUD	MARIPOSA WWTP	CA0079430	Q
MAXWELL P.U.D.	MAXWELL PUD WWTP	CA0079987	Q
MERCED, CITY OF	MERCED WWTP	CA0079219	M
MIRANT DELTA LLC	CONTRA COSTA POWER PLT ANTIOCH	CA0004863	M
MODESTO ID	MODESTO ID REGIONAL WTP	CA0083801	Q
MODESTO, CITY OF	GRAYSON PARK WELL NO.295	CA0083054	Q
MODESTO, CITY OF	MODESTO WWTP	CA0079103	M
MOUNTAIN HOUSE CSD	MOUNTAIN HOUSE WWTP	CA0084271	M
MT LASSEN TROUT FARMS INC	MEADOWBROOK FACILITY	CA0080373	Q
NEVADA CITY, CITY OF	NEVADA CITY WWTP	CA0079901	Q
NEVADA CO SD #1	CASCADE SHORES WWTP	CA0083241	Q
NEVADA CO SD #1	LAKE OF THE PINES WWTP	CA0081612	Q
NEVADA CO SD #1	LAKE WILDWOOD WWTP	CA0077828	M
OLIVEHURST PUD	OLIVEHURST WWTP	CA0077836	M
ORIGINAL SIXTEEN TO ONE MINE	SIXTEEN TO ONE MINE	CA0081809	Q
OROVILLE WYANDOTTE ID	MINERS RANCH WTP	CA0083143	B
PACIFIC COAST SPROUT FARMS	SACRAMENTO FACILITY	CA0082961	Q
PACTIV CORP	PACTIV MOLDED PULP MILL	CA0004821	M
PARADISE ID	PARADISE WTP	CA0083488	B
PLACER CO FACILITY SERVICES 1	PLACER CO SMD NO 1	CA0079316	M
PLACER CO FACILITY SERVICES 1	PLACER CO SMD NO 3	CA0079367	Q
PLACER CO FACILITY SERVICES 1	SA NO 28, ZONE NO.6	CA0079341	Q
PLACERVILLE, CITY OF	HANGTOWN CREEK WWTP	CA0078956	M

Table A.1: NPDES-Permitted Facilities Required to Conduct Effluent Methylmercury Monitoring under California Water Code Section 13267.

AGENCY NAME	FACILITY NAME	NPDES NO	MONITORING FREQUENCY [(a)]
PLANADA CSD	WWTP	CA0078950	Q
PROCTER AND GAMBLE COMPANY	PROCTER & GAMBLE CO WWTP	CA0004316	Q
RED BLUFF, CITY OF	RED BLUFF WWTP	CA0078891	M
REDDING, CITY OF	CLEAR CREEK WWTP	CA0079731	M
REDDING, CITY OF	STILLWATER WWTP	CA0082589	M
RIO ALTO WD	LAKE CALIFORNIA WWTP	CA0077852	B
RIO VISTA, CITY OF	RIO VISTA WWTP	CA0079588	Q
RIO VISTA, CITY OF	TRILOGY WWTP	CA0083771	Q
RIVER HIGHLANDS CSD	HAMMONTON GOLD VILLAGE WWTP	CA0081574	Q
RIVIERA WEST MUTUAL WATER CO	RIVIERA WEST WATER SUPPLY TP	CA0083925	Q
ROSEVILLE, CITY OF	DRY CREEK WWTP	CA0079502	M
ROSEVILLE, CITY OF	PLEASANT GROVE WWTP	CA0084573	M
S.M.U.D.	RANCHO SECO NUCLEAR GEN STA 1	CA0004758	M
SACRAMENTO CO AIRPORT SYSTEM	SACRAMENTO INTERNATIONAL AIRPT	CA0034841	Q
SACRAMENTO COGENERATION AUTH.	PROCTOR & GAMBLE COGEN. PLANT	CA0083569	Q
SACRAMENTO MUNICIPAL UTILITY D	SMUD COGENERATION PLANT	CA0083658	Q
SACRAMENTO REGIONAL CSD-ELK GV	WALNUT GROVE WWTP	CA0078794	Q
SACRAMENTO, CITY OF	COMBINED WW COLLECTION/TRT SYS	CA0079111	M
SAN ANDREAS SANITARY DIST.	SAN ANDREAS WWTP	CA0079464	Q
SAN JOAQUIN CO DPW	CSA 31 - FLAG CITY WWTP	CA0082848	Q
SEWER COMM - OROVILLE REGION	OROVILLE WWTP	CA0079235	M
SHASTA CSA #17	COTTONWOOD WWTP	CA0081507	Q
SHASTA LAKE, CITY OF	SHASTA LAKE WTP	CA0004693	B
SHASTA LAKE, CITY OF	SHASTA LAKE WWTP	CA0079511	Q
SHEA, J F COMPANY INC	FAWNDALE ROCK & ASPHALT	CA0083097	B
SIERRA PACIFIC INDUSTRIES	CAMINO SAWMILL	CA0078841	Q
SIERRA PACIFIC INDUSTRIES	MARTELL COMPLEX/SIERRA PINE	CA0004219	Q
SIERRA PACIFIC INDUSTRIES	SIERRA PACIFIC, ANDERSON DIV	CA0082066	Q
SIERRA PACIFIC INDUSTRIES	SIERRA PACIFIC, SHASTA LAKE DV	CA0081400	Q
STIMPEL-WIEBELHAUS ASSOCIATES	SWA AT MOUNTAIN GATE	CA0084140	B
STOCKTON COGENERATION COMPANY	STOCKTON COGENERATION FACILITY	CA0081965	Q
STOCKTON, CITY OF	STOCKTON WWTP	CA0079138	M
THE BOEING COMPANY	INTERIM GW TREATMENT SYSTEM	CA0084891	B
TRACY, CITY OF	TRACY WWTP	CA0079154	M
TUOLUMNE UD/JAMESTOWN SD	SONORA WWTP/JAMESTOWN WWTP	CA0084727	M
TURLOCK, CITY OF	TURLOCK WWTP	CA0078948	M
U.A. LOCAL 38 TRUST FUND	KONOCTI HARBOR INN	CA0083551	Q
U.S. BUREAU OF RECLAMATION	SLIGER MINE	CA0084905	Q
UNIVERSITY OF CALIFORNIA, DAVIS	AQUATIC CENTER/ANIMAL SCIENCE	CA0083348	Q

Table A.1: NPDES-Permitted Facilities Required to Conduct Effluent Methylmercury Monitoring under California Water Code Section 13267.

AGENCY NAME	FACILITY NAME	NPDES NO	MONITORING FREQUENCY [a]
UNIVERSITY OF CALIFORNIA, DAVIS	HYDRAULICS LABORATORY	CA0084182	Q
UNIVERSITY OF CALIFORNIA, DAVIS	UC DAVIS WWTP	CA0077895	M
UNITED AUBURN INDIAN COMMUNITY	AUBURN RANCHERIA CASINO WWTP	CA0084697	Q
US AIR FORCE - BEALE AFB	BEALE AFB WWTP	CA0110299	B
US AIR FORCE - MCCLELLAN AFB	GW EXTR & TRMT SYSTEM	CA0081850	B
US DEPT OF AGRICULTURE	UCD AQUATIC WEED LABORATORY	CA0083364	Q
USDI BUREAU OF RECLAMATION	WINTER RUN REARING FACILITY	CA0084298	Q
USDI FISH & WILDLIFE SERVICE	COLEMAN FISH HATCHERY	CA0004201	Q
VACAVILLE, CITY OF	EASTERLY WWTP	CA0077691	M
WASTE MANAGEMENT OF ALAMEDA CO	ALTAMONT LANDFILL & RESOURCE	CA0083763	Q
WEST SACRAMENTO, CITY OF	WEST SACRAMENTO WWTP	CA0079171	M
WHEELABRATOR SHASTA ENERGY CO	WHEELABRATOR SHASTA ENERGY CO	CA0081957	Q
WILLIAMS, CITY OF	WILLIAMS WWTP	CA0077933	Q
WILLOWS, CITY OF	WILLOWS WWTP	CA0078034	M
WOODLAND, CITY OF - DOMESTIC	WOODLAND WWTP	CA0077950	M
YUBA CITY	YUBA CITY WWTP	CA0079260	M
YUBA CWD	FORBESTOWN WTP	CA0084824	B

[a] Key: Biannual (B); Monthly (M); and Quarterly (Q).
[b] The Manteca Aggregate Sand Plant is now known as Oakwood Lake Subdivision Mining Reclamation.

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APPENDIX B
SUMMARY OF NPDES FACILITY EFFLUENT AND INFLUENT METHYLMERCURY AND TOTAL MERCURY CONCENTRATIONS

Many facilities have multiple discharge locations and influent sources (intakes). Therefore, there are separate tables that summarize the methylmercury concentrations for each discharge and intake:

- Table B.1: Summary of Effluent 1 and Effluent 2 Methylmercury Concentrations
- Table B.2: Summary of Effluent 3 and Effluent 4 Methylmercury Concentrations
- Table B.3: Summary of Influent/Intakes 1 and 2 Methylmercury Concentrations
- Table B.4: Summary of Influent/Intakes 3 and 4 Methylmercury Concentrations

Table B.1: Summary of Effluent 1 and Effluent 2 Methylmercury Concentrations

Facility	Footnotes	# of EFF 1 MeHg Samples	# of EFF 1 Nondetect Samples	Ave. EFF 1 MeHg Conc. (ng/l) (p)	Min. EFF 1 MeHg Conc (ng/l)	Max. EFF 1 MeHg Conc (ng/l)	# of EFF 2 MeHg Samples	# of EFF 2 Nondetect Samples	Ave. EFF 2 MeHg Conc. (ng/l) (p)	Min. EFF 2 MeHg Conc (ng/l)	Max. EFF 2 MeHg Conc (ng/l)
Aggregate											
Crystal Creek Aggregate	a	1	1	0.010	0.010	0.010					
J.F. Shea CO Fawndale Rock and Asphalt	a	1	1	0.010	0.010	0.010	1	1	0.010	0.010	0.010
Lehigh Southwest Cement Co.	a, b	1	1	0.010	0.010	0.010	1	1	0.010	0.010	0.010
Oakwood Lake Subdivision Mining Reclamation	a	2	1	0.027	0.010	0.043					
Stimpel Wiebelhaus Assoc. SWA at Mountain Gate		1		0.081	0.081	0.081					
Aquaculture											
Calaveras Trout Farm (Rearing Facility)		2		0.060	0.027	0.092					
DFG Darrah Springs Fish Hatchery	a, c	4	1	0.024	0.010	0.031	4	1	0.028	0.010	0.043
DFG Merced River Fish Hatchery		1		0.037	0.037	0.037					
DFG Moccasin Creek Fish Hatchery	a	1	1	0.010	0.010	0.010					
DFG Mokelumne River Fish Hatchery	a	4	1	0.041	0.010	0.059					
DFG Nimbus Fish Hatchery		3		0.065	0.053	0.085	1		0.129	0.129	0.129
DFG San Joaquin Fish Hatchery		2		0.060	0.047	0.073					
Pacific Coast Sprout Farms (Sacramento Facility)	a	1	1	0.010	0.010	0.010					
UC Davis Center for Aquatic Biology & Aquaculture	a, d	4	2	0.030	0.010	0.067	4	1	0.082	0.010	0.243
USDI BR Winter Run Rearing Facility	a	4	4	0.010	0.010	0.010					
USDI FWS Coleman Fish Hatchery		3		0.030	0.023	0.043					
Drinking Water Treatment											
Bella Vista Water District		1		0.027	0.027	0.027					
Clear Creek CSD WTP		2		0.036	0.028	0.043	1		0.041	0.041	0.041
Modesto ID Regional WTP	k	3 [2]		0.056	0.045	0.066					
Paradise Irrigation District	a	1	1	0.013	0.013	0.013					
Shasta Lake WTP	a	2	1	0.025	0.010	0.040					
South Feather Water & Power Agency Miners Ranch WTP	a, k	2 [1]	2 [1]	0.013	0.013	0.013					

Table B.1: Summary of Effluent 1 and Effluent 2 Methylmercury Concentrations

Facility	Footnotes	# of EFF 1 MeHg Samples	# of EFF 1 Nondetect Samples	Ave. EFF 1 MeHg Conc. (ng/l) (p)	Min. EFF 1 MeHg Conc (ng/l)	Max. EFF 1 MeHg Conc (ng/l)	# of EFF 2 MeHg Samples	# of EFF 2 Nondetect Samples	Ave. EFF 2 MeHg Conc. (ng/l) (p)	Min. EFF 2 MeHg Conc (ng/l)	Max. EFF 2 MeHg Conc (ng/l)
Food Processing											
Bell Carter Olive Company Inc.	a	4	2	0.017	0.010	0.027					
CA Dairies, Inc. Los Banos Foods	a	4	3	0.016	0.013	0.026					
Hershey Chocolate USA, Oakdale	a	4	4	0.010	0.010	0.010					
Groundwater Remediation											
Aerojet Interim GW WTP	a, k	2 [1]	2 [1]	0.013	0.013	0.013	1	1	0.013	0.013	0.013
Boeing Company Interim Treat. System	a	1	1	0.010	0.010	0.010					
Defense Logistics Agency Sharpe GW Cleanup	a, i	3	2	0.018	0.010	0.033	1	1	0.010	0.010	0.010
General Electric Co. GWCS	a, j, m	3	3	0.010	0.010	0.010	3	3	0.010	0.010	0.010
Heating/Cooling											
Aerojet Sacramento Facility	f, k	1 [0]		(k)	(k)	(k)					
CA (State of) Central Heating/Cooling Facility	a	4	3	0.015	0.010	0.029					
CALAMCO - Stockton Terminal		4		0.293	0.030	0.919					
Gaylord Container Corp. Antioch Pulp and Paper Mill		3		0.055	0.048	0.061					
Sacramento International Airport		2		0.035	0.023	0.046					
UA Local 38 Trust Fund Konocti Harbor Resort		1		0.079	0.079	0.079					
Manufacturing											
Formica Corporation Sierra Plant		1		0.050	0.050	0.050					
Proctor & Gamble Co. WWTP	a, e	3	3	0.010	0.010	0.010	1		0.033	0.033	0.033
Mines											
Sliger Mine	a	4	1	0.064	0.025	0.091					
Miscellaneous											
DGS Office of State Publishing	a, k	4 [3]	4 [3]	0.010	0.010	0.010					
UC Davis Hydraulics Laboratory		3		0.057	0.038	0.082					
Municipal WWTPs											
Anderson WWTP	a	12	2	0.090	0.010	0.271					

Table B.1: Summary of Effluent 1 and Effluent 2 Methylmercury Concentrations

Facility	Footnotes	# of EFF 1 MeHg Samples	# of EFF 1 Nondetect Samples	Ave. EFF 1 MeHg Conc. (ng/l) (p)	Min. EFF 1 MeHg Conc (ng/l)	Max. EFF 1 MeHg Conc (ng/l)	# of EFF 2 MeHg Samples	# of EFF 2 Nondetect Samples	Ave. EFF 2 MeHg Conc. (ng/l) (p)	Min. EFF 2 MeHg Conc (ng/l)	Max. EFF 2 MeHg Conc (ng/l)
Atwater WWTP	a	12	3	0.034	0.010	0.084					
Auburn WWTP	a	12	6	0.028	0.010	0.072					
Biggs WWTP		2		1.605	0.150	3.060					
Brentwood WWTP	a	13	13	0.010	0.010	0.010					
Canada Cove LP French Camp Golf & RV Park WWTP		4		0.147	0.029	0.291					
Chico Regional WWTP		12		0.126	0.057	0.178					
Colfax WWTP		3		0.197	0.115	0.350					
Colusa WWTP		4		2.863	1.970	4.020					
Corning Industries/ Domestic WWTP	k	3 [2]		0.044	0.034	0.053					
Cottonwood WWTP		5		0.096	0.045	0.245					
Davis WWTP	o	7		0.546	0.305	1.040	5		0.613	0.247	1.440
Deer Creek WWTP	a	13	11	0.015	0.013	0.032					
Deuel Vocational Institute WWTP	a, k	4 [3]	4 [3]	0.010	0.010	0.010					
Discovery Bay WWTP	a	12	7	0.191	0.013	2.030					
El Dorado Hills WWTP	a, k, l	13 [12]	10	0.018	0.013	0.055	2	2	0.013	0.013	0.013
Galt WWTP		6		0.139	0.027	0.220					
Grass Valley WWTP	a	16	2	0.160	0.010	0.938					
Jackson WWTP		4		0.108	0.061	0.161					
Lincoln WWTP	a, k	8 [7]	6	0.018	0.010	0.068					
Live Oak WWTP		4		0.591	0.427	0.785					
Lodi White Slough WWTP	a, n	12	4	0.128	0.010	1.240					
Manteca WWTP		11		0.216	0.037	0.356					
Mariposa PUD WWTP		4		0.393	0.040	0.912					
Maxwell PUD WWTP		4		0.993	0.044	1.720					
Merced WWTP		12		0.386	0.130	0.672					
Modesto WWTP		9		0.130	0.108	0.170					

Table B.1: Summary of Effluent 1 and Effluent 2 Methylmercury Concentrations

Facility	Footnotes	# of EFF 1 MeHg Samples	# of EFF 1 Nondetect Samples	Ave. EFF 1 MeHg Conc. (ng/l) (p)	Min. EFF 1 MeHg Conc (ng/l)	Max. EFF 1 MeHg Conc (ng/l)	# of EFF 2 MeHg Samples	# of EFF 2 Nondetect Samples	Ave. EFF 2 MeHg Conc. (ng/l) (p)	Min. EFF 2 MeHg Conc (ng/l)	Max. EFF 2 MeHg Conc (ng/l)
Nevada City WWTP	a	4	2	0.048	0.010	0.146					
Nevada Co SD #1 Cascade Shores WWTP	a	3	1	0.142	0.010	0.286					
Nevada Co SD #1 Lake Wildwood WWTP	a	12	1	0.109	0.010	0.320					
Nevada Co SD #2 Lake of the Pines WWTP		2		1.409	0.708	2.110					
Olivehurst PUD WWTP	a	13	1	0.144	0.013	0.268					
Oroville WWTP		12		0.147	0.061	0.280					
Placer Co. SA #28 Zone #6 WWTP		2		0.668	0.474	0.862					
Placer Co. SMD #1 WWTP		12		0.141	0.042	0.350					
Placer Co. SMD #3 WWTP		12		0.100	0.037	0.381					
Placerville Hangtown Creek WWTP	a	12	1	0.058	0.013	0.170					
Planada Comm. Service Dist. WWTP		4		1.168	0.374	2.040					
Red Bluff WWTP	a	12	6	0.027	0.010	0.057					
Redding Clear Creek WWTP	a	12	3	0.042	0.013	0.084					
Redding Stillwater WWTP	a	12	12	0.013	0.013	0.013					
Rio Alto WD- Lake CA WWTP		2		1.746	0.141	3.350					
Rio Vista Main WWTP		4		0.164	0.035	0.522					
Roseville Dry Creek WWTP	a	12	4	0.023	0.010	0.055					
Roseville Pleasant Grove WWTP	a	12	10	0.017	0.010	0.070					
San Andreas SD WWTP		4		0.249	0.178	0.293					
San Joaquin Co DPW - Flag City WWTP	a	3	1	0.081	0.013	0.152					
Shasta Lake WWTP	a	2	1	0.022	0.010	0.034					
SRCSD Sacramento River WWTP		108		0.613	0.118	1.640					
SRCSD Walnut Grove WWTP (CSD1)	k	3 [2]		2.155	0.949	3.360					
Stockton WWTP	a	12	1	0.935	0.010	2.090					
Tracy WWTP	a	13	1	0.145	0.013	0.422					
Tuolumne UD Sonora WWTP/ Jamestown WWTP		3		0.182	0.071	0.262					

Table B.1: Summary of Effluent 1 and Effluent 2 Methylmercury Concentrations

Facility	Footnotes	# of EFF 1 MeHg Samples	# of EFF 1 Nondetect Samples	Ave. EFF 1 MeHg Conc. (ng/l) (p)	Min. EFF 1 MeHg Conc (ng/l)	Max. EFF 1 MeHg Conc (ng/l)	# of EFF 2 MeHg Samples	# of EFF 2 Nondetect Samples	Ave. EFF 2 MeHg Conc. (ng/l) (p)	Min. EFF 2 MeHg Conc (ng/l)	Max. EFF 2 MeHg Conc (ng/l)
Turlock WWTP	a, g	12	1	0.059	0.010	0.079					
UC Davis WWTP	a	12	3	0.038	0.010	0.078					
United Auburn Indian Community Casino WWTP	a	2	2	0.010	0.010	0.010					
Vacaville Easterly WWTP	a	12	4	0.024	0.010	0.057					
West Sacramento WWTP	a	12	1	0.050	0.010	0.085					
Williams WWTP		4		1.553	0.560	2.100					
Woodland WWTP	a	12	2	0.031	0.013	0.059					
Yuba City WWTP		12		0.295	0.106	0.625					
Paper & Saw Mills											
Pactiv Molded Pulp Mill	a	12	5	0.039	0.010	0.085					
SPI Anderson Division		4		0.106	0.036	0.140	3		0.120	0.052	0.177
SPI Shasta Lake							2		0.607	0.023	1.190
Power Generation											
Calpine Corp. Greenleaf Unit One Cogen Plant		4		0.064	0.020	0.117					
Camanche Dam Powerhouse	a	4	3	0.020	0.010	0.039					
GWF Power Systems	a	4	4	0.013	0.013	0.013					
Mirant Delta CCPP	h	12		0.075	0.020	0.121	10		0.086	0.042	0.150
Sacramento Cogen Authority Procter & Gamble Plant	a	4	1	0.052	0.013	0.070					
Stockton Congeneration Co.	a	4	3	0.017	0.013	0.029					
Wheelabrator Shasta Energy Co.		4		0.104	0.055	0.178					
Power Generation/ Domestic WWTP											
SMUD Rancho Seco Nuclear Generating Station	a	12	4	0.040	0.013	0.104					

Table B.1 Footnotes:

a. Sample MeHg concentration <MDL; half the detection limit was used for calculations.

b. Lehigh Southwest Cement Co. EFF 1: Outfall #1, Shale Quarry Tunnel Road. Effluent 2: Lehigh Southwest Cement Co., 002B: Shale Quarry

c. Darrah Springs Fish Hatchery EFF 1: Upper Springs. EFF 2: Darrah Springs Fish Hatchery - Lower Springs

d. UCD Center for Aquatic Biology & Aquaculture, EFF 1: CABA Aquatic Center. EFF 2: CABA Putah Creek Facility

e. Proctor & Gamble, Pond EFF 2: Effluent PTI-660

f. Aerojet Sacramento Facility, EFF 1 Sample collected from West Detention Pond because there was no discharge to the American River during the rainy season.

g. City of Turlock WWTP, EFF 1: R5

h. Mirant Delta CCPP EFF 1:Outfall 001, EFF 2: Outfall 002

i. Defense Logistics Agency, Sharp Groundwater Cleanup; EFF 1: CBCGWTPEFF = Central Area B/C Aquifer Zone, EFF 2: NBGWTPEFF = North GWTP effluent

j. General Electric Co., GWCS: EFF 1: Air Stripper Effluent, EFF 2: 100-foot Zone Effluent

k. Results for the following facilities and sample dates were not incorporated in the calculations due to sample preservation hold times exceeding EPA recommendations: Aerojet Interim GW WTP (18 November 2005, EFF 1 and EFF 2 were both <MDL); Aerojet Sacramento Facility (18 March 2005, 0.057 ng/l); Corning Industries/ Domestic WWTP (22 September 2004, 0.041 ng/l); Deuel Vocational Institute WWTP (26 October 2004, <MDL); DGS Office of State Publishing (8 July 2005, <MDL); El Dorado Hills WWTP (9 August 2005, 0.057 ng/l); Lincoln WWTP (25 August 2005, 0.034 ng/l); Modesto ID Regional WWTP (8 October 2004, 0.038 ng/l); South Feather Water & Power Agency Miners Ranch WTP (9 September 2004, <MDL); and SRCSD Walnut Grove WWTP (CSD1) (29 December 2004, 0.759 ng/l).

l. El Dorado Hills WWTP sampled effluent when discharging to land and to surface water. Only samples collected when the plant discharged to surface water (December 2004 through April 2005) were used in the February 2008 Delta TMDL Report (Wood *et al.*, 2008b). However, this summary includes samples that were collected when the plant discharged to land and to surface water.

m. General Electric Co. GWCS conducted four sampling events. However, results for samples collected on 8 October 2004 were not incorporated in the calculations due to sample contamination with mercury in the laboratory and preservation hold times at the laboratory exceeding EPA recommendations.

n. Lodi White Slough WWTP sampled effluent when discharging to land and to surface water. Only samples collected when the plant discharged to surface water (September 2004 through June 2005) were used in the TMDL Report. However, this summary includes samples that were collected when the plant discharged to land and to surface water.

o. Davis WWTP: EFF 1: Willow Slough, EFF 2: Conaway Ranch Toe Drain in the Yolo Bypass

p. Tables 6.5 and 8.4 in the main text of the February 2008 TMDL Report and Tables B and C in the draft Basin Plan amendment provide average concentration values rounded to two decimal places based on un-rounded calculations. For example, the Tracy WWTP had an average methylmercury concentration of 0.014465 ng/l, which rounds to 0.0145 ng/l in this table, and 0.14 ng/l in Table 6.5.

Table B.2: Summary of Effluent 3 and Effluent 4 Methylmercury Concentrations

Facility	Footnotes	# of EFF 3 MeHg Samples	# of EFF 3 Nondetect Samples	Ave. EFF 3 MeHg Conc. (ng/l)	Min. EFF 3 MeHg Conc. (ng/l)	Max. EFF 3 MeHg Conc. (ng/l)	# of EFF 4 MeHg Samples	# of EFF 4 Nondetect Samples	Ave. EFF 4 MeHg Conc. (ng/l)	Min. EFF 4 MeHg Conc. (ng/l)	Max. EFF 4 MeHg Conc. (ng/l)
Aggregate											
Lehigh Southwest Cement Co.	a, b	1	1	0.010	0.010	0.010	1		0.062	0.062	0.062
Groundwater Remediation											
Aerojet Interim GW WTP	a, e	2 [1]	2 [1]	0.013	0.013	0.013	2 [1]	2 [1]	0.013	0.013	0.013
Defense Logistics Agency Sharpe GW Cleanup	a, c	2	2	0.010	0.010	0.010					
General Electric Co. GWCS	a, d, f	3	3	0.010	0.010	0.010					

a. Sample MeHg concentration <MDL; half the detection limit was used for calculations.
b. Lehigh Southwest Cement Co., EFF 3: 001A: Limestone Quarry, EFF 4: 00X: Cement Plant
c. Defense Logistics Agency, Sharp Groundwater Cleanup, EFF 3: SBGWTPEFF= South GWTP effluent, EFF 4: SSJCUPST = South San Joaquin Irrigation District Canal (upstream sample).
d. General Electric Co. EFF 3: GWCS: Multizone Effluent
e. Aerojet Interim Groundwater WTP results for samples collected on 18 November 2005 (both <MDL) were not incorporated in the calculations due to sample preservation hold time exceeding EPA recommendations.
f. General Electric Co. GWCS conducted four sampling events. However, results for General Electric Co. GWCS samples collected on 8 October 2004 were not incorporated in the calculations due to sample contamination with mercury in the laboratory and preservation hold times at the laboratory exceeding EPA recommendations.

Table B.3: Summary of Influent/Intakes 1 and 2 Methylmercury Concentrations

Facility	Footnotes	# of INF 1 MeHg Samples	# of INF 1 Nondetect Samples	Ave. INF 1 MeHg Conc. (ng/l)	Min. INF 1 MeHg Conc. (ng/l)	Max. INF 1 MeHg Conc. (ng/l)	# of INF 2 MeHg Samples	# of INF 2 Nondetect Samples	Ave. INF 2 MeHg Conc. (ng/l)	Min. INF 2 MeHg Conc. (ng/l)	Max. INF 2 MeHg Conc. (ng/l)
Aquaculture											
Calaveras Trout Farm (Rearing Facility)		1		0.067	0.067	0.067					
DFG Darrah Springs Fish Hatchery	a, b	1	1	0.010	0.010	0.010	1	1	0.010	0.010	0.010
DFG Mokelumne River Fish Hatchery	a	1	1	0.010	0.010	0.010					
DFG Nimbus Fish Hatchery		2		0.052	0.051	0.052	1		0.031	0.031	0.031
DFG San Joaquin Fish Hatchery		1		0.021	0.021	0.021					
Drinking Water Treatment											
Bella Vista Water District		1		0.084	0.084	0.084					
Modesto ID Regional WTP	a, h	3 [2]	2 [1]	0.022	0.010	0.033					
Groundwater Remediation											
General Electric Co. GWCS	a, g	3	3	0.010	0.010	0.010	3	3	0.010	0.010	0.010
Heating/Cooling											
CALAMCO - Stockton Terminal		1		0.026	0.026	0.026					
Manufacturing											
Proctor & Gamble Co. WWTP	a, c	3	3	0.010	0.010	0.010	3	2	0.015	0.010	0.026
Municipal WWTPs											
Atwater WWTP		1		1.940	1.940	1.940					
Auburn WWTP		1		2.720	2.720	2.720					
Chico Regional WWTP		11		1.167	0.527	1.590					
Colusa WWTP		1		1.580	1.580	1.580					
Davis WWTP	d	1		1.660	1.660	1.660					
Deer Creek WWTP		13		1.154	0.335	1.570					
El Dorado Hills WWTP	h	13 [12]		1.139	0.388	2.020					
Grass Valley WWTP		16		1.897	0.588	5.010					
Jackson WWTP		1		0.854	0.854	0.854					
Lodi White Slough WWTP		12		1.396	0.730	2.740					

Table B.3: Summary of Influent/Intakes 1 and 2 Methylmercury Concentrations

Facility	Footnotes	# of INF 1 MeHg Samples	# of INF 1 Nondetect Samples	Ave. INF 1 MeHg Conc. (ng/l)	Min. INF 1 MeHg Conc. (ng/l)	Max. INF 1 MeHg Conc. (ng/l)	# of INF 2 MeHg Samples	# of INF 2 Nondetect Samples	Ave. INF 2 MeHg Conc. (ng/l)	Min. INF 2 MeHg Conc. (ng/l)	Max. INF 2 MeHg Conc. (ng/l)
Mariposa PUD WWTP		1		0.068	0.068	0.068					
Maxwell PUD WWTP		1		14.600	14.600	14.600					
Nevada City WWTP		4		3.140	1.090	6.230					
Placer Co. SMD #1 WWTP		1		2.590	2.590	2.590					
Planada Comm. Service Dist. WWTP		1		3.390	3.390	3.390					
Rio Vista Main WWTP		4		2.903	1.570	4.790					
Roseville Dry Creek WWTP		9		1.360	0.600	2.860					
Roseville Pleasant Grove WWTP		9		0.808	0.120	2.160					
SRCSD Sacramento River WWTP		111		1.624	0.746	2.840					
SRCSD Walnut Grove WWTP (CSD1)	h	3 [2]		3.683	0.626	6.740					
UC Davis WWTP		12		2.991	0.074	11.100					
Williams WWTP		4		7.133	4.530	11.900					
Woodland WWTP		12		2.309	0.767	7.070					
Power Generation											
Camanche Dam Powerhouse	e	1		0.095	0.095	0.095					
GWF Power Systems	a	4	3	0.075	0.013	0.263					
Mirant Delta CCPP	a, f	12	1	0.096	0.010	0.296					
Sacramento Cogen Authority Procter & Gamble Plant	a	4	3	0.029	0.010	0.080					

a. Sample MeHg concentration <MDL; half the detection limit was used for calculations.
b. Darrah Springs Fish Hatchery, INF 1 & 2 Upper Springs
c. Proctor & Gamble, INF 2: Well #2 BR-226
d. City of Davis Plant, INF 1 -Head: Influent coming to the plant, collected at head-gate
e. Camache Dam Powerhouse, INF 1: receiving water received 200 feet upstream of discharge
f. Mirant Delta CCPP, INF 1: Intake 002
g. General Electric Co., INF 1: GWCS: Air Stripper Influent, INF 2: 100-foot Zone Influent. General Electric Co. GWCS conducted four sampling events. However, results for General Electric Co. GWCS samples collected on 8 October 2004 were not incorporated in the calculations due to sample contamination with mercury in the laboratory and preservation hold times at the laboratory exceeding EPA recommendations.
h. Results for the following facilities and sample dates were not incorporated in the calculations due to sample preservation hold times exceeding EPA recommendations: El Dorado Hills WWTP (9 August 2005, 1.41 ng/l); Modesto ID Regional WWTP (8 October 2004, <MDL); and SRCSD Walnut Grove WWTP (CSD1) (29 December 2004, 1.15 ng/l).

Table B.4: Summary of Influent/Intakes 3 and 4 Methylmercury Concentrations

Facility	Footnotes	# of INF 3 MeHg Samples	# of INF 3 Nondetect Samples	Ave. INF 3 MeHg Conc. (ng/l)	Min. INF 3 MeHg Conc. (ng/l)	Max. INF 3 MeHg Conc. (ng/l)	# of INF 4 MeHg Samples	# of INF 4 Nondetect Samples	Ave. INF 4 MeHg Conc. (ng/l)	Min. INF 4 MeHg Conc. (ng/l)	Max. INF 4 MeHg Conc. (ng/l)
Groundwater Remediation											
General Electric Co. GWCS	a, c	3	3	0.010	0.010	0.010					
Manufacturing											
Proctor & Gamble Co. WWTP	a, b	3	3	0.010	0.010	0.010	3	3	0.010	0.010	0.010

a. Sample MeHg concentration <MDL; half the detection limit was used for calculations.
b. Proctor & Gamble, INF 3: Well #3 BR-2025, INF 4:Well #4 BRL-341
c. General Electric Co., INF 3: Multizone Influent. General Electric Co. GWCS conducted four sampling events. However, results for General Electric Co. GWCS samples collected on 8 October 2004 were not incorporated in the calculations due to sample contamination with mercury in the laboratory and preservation hold times at the laboratory exceeding EPA recommendations.

Table B.5: Summary of Facility Discharge Volumes and Effluent Total Mercury and Methylmercury Concentrations and Loads

Facility	NPDES No.	Facility Type	Proximity to Delta / Yolo Bypass [a]	Delta Subarea that Receives Discharge	NPDES Permit Rescinded During or After TMDL Study Period	NPDES Permit Rescision Date	Discharged in Sept. 2009 d/s Major Dams	Include in Sum of MeHg Source Loads d/s Major Dams for TMDL Period	Include in Sum of TotHg Source Loads d/s Major Dams for 20-yr Period	Annual Discharge (mgd)	Annual Discharge Type	Maximum Level of Mun. WWTP Treatment When EFF TotHg Data Were Collected	Treatment Category for Mun WWTPs d/s Major Dams w/o EFF TotHg Data	Ave. EFF TotHg Conc. [b] (ng/l)	EFF TotHg Load (g/yr)	Ave. EFF MeHg Conc. [b] (ng/l)	Treatment Category for EFF MeHg Conc. Estimate	EFF MeHg Load (g/yr)
Aerojet Interim GW WTP	CA0083861	WTP (GW)	U/S of Delta / Yolo Bypass	Sacra-mento			X	X	X	5.00	average			2.6*	18	0.013		0.090
Aerojet Sacramento Facility WWTP	CA0004111	Heating / Cooling	U/S of Delta / Yolo Bypass	Sacra-mento			X			0.024	WY2005					0.057		
AFB Conversion Agency A C & W GW Treatment	CA0083992	WTP (GW)	U/S of Delta / Yolo Bypass	Sacra-mento			X	X	X	0.39	average			2.6*	1.4	0.013		0.0070
Agricultural Mgmt & Production Afterthought Mine	CA0084166	Mines	U/S of Delta / Yolo Bypass	Sacra-mento			X	X	X	0.054	peak flow					0.064*	Mines	0.0048
Altamont Landfill and Resource	CA0083763	Landfill	U/S of Delta / Yolo Bypass	San Joaquin	X	Jun-07			X	0.15	(c)			23.1				
Anderson WWTP	CA0077704	Mun. WWTP	U/S of Delta / Yolo Bypass	Sacra-mento			X	X	X	1.4	dry weather average		Tertiary	4.1*	7.9	0.090		0.17
Atwater WWTP	CA0079197	Mun. WWTP	U/S of Delta / Yolo Bypass	San Joaquin			X	X	X	3.4	dry weather average		Secondary	8.7*	41	0.034		0.16
Auburn WWTP	CA0077712	Mun. WWTP	U/S of Delta / Yolo Bypass	Sacra-mento			X	X	X	1.17	WY2005	Tertiary		1.5	2.4	0.028		0.045
Beale Air Force Base WWTP	CA0110299	Mun. WWTP	U/S of Delta / Yolo Bypass	Sacra-mento			X	X	X	0.7	baseline	Secondary		15.9	15	0.105*	Mun WWTP: Filtration + Chlor./ Dechlor.	0.10
Bell Carter Olive Company Inc.	CA0083721	Food	U/S of Delta / Yolo Bypass	Sacra-mento			X	X	X	0.38	maximum flow allowed					0.017		0.0089
Bell Carter Olive Company Inc. Plant 1	CA0081639	Food	U/S of Delta / Yolo Bypass	Sacra-mento			X	X	X	0.15	baseline					0.014*	Food	0.0029

Table B.5: Summary of Facility Discharge Volumes and Effluent Total Mercury and Methylmercury Concentrations and Loads

Facility	NPDES No.	Facility Type	Proximity to Delta / Yolo Bypass [a]	Delta Subarea that Receives Discharge	NPDES Permit Rescinded During or After TMDL Study Period	NPDES Permit Rescinsion Date	Discharged in Sept. 2009 d/s Major Dams	Include in Sum of MeHg Source Loads d/s Major Dams for TMDL Period	Include in Sum of TotHg Source Loads d/s Major Dams for 20-yr Period	Annual Discharge (mgd)	Annual Discharge Type	Maximum Level of Mun. WWTP Treatment When EFF TotHg Data Were Collected	Treatment Category for Mun WWTPs d/s Major Dams w/o EFF TotHg Data	Ave. EFF TotHg Conc. [b] (ng/l)	EFF TotHg Load (g/yr)	Ave. EFF MeHg Conc. [b] (ng/l)	Treatment Category for EFF MeHg Conc. Estimate	EFF MeHg Load (g/yr)
Bella Vista Water District	CA0080799	Water Filtration	U/S of Delta / Yolo Bypass	Sacra-mento			X	X	X	0.5	baseline			4.6*	3.200	0.027		0.019
Biggs WWTP	CA0078930	Mun. WWTP	U/S of Delta / Yolo Bypass	Sacra-mento			X	X	X	0.38	average		Secondary	8.7*	4.6	1.605		0.84
Boeing Company, Interm. Treat. System	CA0084891	WTP (GW)	U/S of Delta / Yolo Bypass	Sacra-mento			X	X	X	0.56	WY2005			2.6*	5.2	0.010		0.0077
Brentwood WWTP	CA0082660	Mun. WWTP	Delta/Yolo Bypass	Marsh Creek			X	X	X	3.09	WY2005	Tertiary		1.3	5.5	0.010		0.086
CA Dairies, Inc. Los Banos Foods	CA0082082	Food	U/S of Delta / Yolo Bypass	San Joaquin	X	Oct-07		X	X	0.5						0.016		0.011
CALAMCO - Stockton Terminal	CA0083968	Heating / Cooling	Delta/Yolo Bypass	Central	X	Oct-06				5.06	WY2005			6.6		0.293		
Calaveras Trout Farm (Rearing Facility)	CA0081752	Aqua-culture	U/S of Delta / Yolo Bypass	San Joaquin			X			19.4	average					0.060		
Calpine Corp. Greenleaf Unit One Cogen Plant	CA0081566	Power	U/S of Delta / Yolo Bypass	Sacra-mento	X	Apr-08				0.11	WY2005			2.3		0.064		
Camache Dam Powerhouse	CA0082040	Power	U/S of Delta / Yolo Bypass	Mokelumne	X	Oct-08				0.04	average			0.8		0.020		
Canada Cove LP French Camp Golf & RV Park WWTP	CA0083682	Mun. WWTP	U/S of Delta / Yolo Bypass	San Joaquin			X	X	X	0.04	average		Tertiary	4.1*	0.23	0.147		0.0081
Chester WWTP	CA0077747	Mun. WWTP	U/S of Major Dam	Sacra-mento								Secondary		8.9				
Chico Regional WWTP	CA0079081	Mun. WWTP	U/S of Delta / Yolo Bypass	Sacra-mento			X	X	X	7.2	average		Secondary	8.7*	86	0.126		1.3
Clear Creek CSD WTP	CA0083828	Water Filtration	U/S of Delta / Yolo Bypass	Sacra-mento			X	X	X	0.16	average			4.6*	1.000	0.036		0.0080
Colfax WWTP	CA0079529	Mun. WWTP	U/S of Major Dam	Sacra-mento						0.024	average seepage rate	Secondary		7.0		0.197		0.0065

Table B.5: Summary of Facility Discharge Volumes and Effluent Total Mercury and Methylmercury Concentrations and Loads

Facility	NPDES No.	Facility Type	Proximity to Delta / Yolo Bypass [a]	Delta Subarea that Receives Discharge	NPDES Permit Rescinded During or After TMDL Study Period	NPDES Permit Rescission Date	Discharged in Sept. 2009 d/s Major Dams	Include in Sum of MeHg Source Loads d/s Major Dams for TMDL Period	Include in Sum of TotHg Source Loads d/s Major Dams for 20-yr Period	Annual Discharge (mgd)	Annual Discharge Type	Maximum Level of Mun. WWTP Treatment When EFF TotHg Data Were Collected	Treatment Category for Mun WWTPs d/s Major Dams w/o EFF TotHg Data	Ave. EFF TotHg Conc. [b] (ng/l)	EFF TotHg Load (g/yr)	Ave. EFF MeHg Conc. [b] (ng/l)	Treatment Category for EFF MeHg Conc. Estimate	EFF MeHg Load (g/yr)
Collins and Aikman	CA0081531	WTP (GW)	U/S of Delta / Yolo Bypass	Yolo Bypass			X	X	X	0.022	average			2.6	0.079	0.013		0.00040
Collins Pine Company Chester Sawmill	CA0004391	Paper Mill / Saw Mills	U/S of Major Dam	Sacra-mento										5.9				
Colusa WWTP	CA0078999	Mun. WWTP	U/S of Delta / Yolo Bypass	Sacra-mento			X	X	X	0.66	WY2005		Secondary	8.7*	7.9	2.863		2.6
Corning Industries/ Domestic WWTP	CA0004995	Mun. WWTP	U/S of Delta / Yolo Bypass	Sacra-mento			X	X	X	1	average		Secondary	8.7*	12	0.044		0.061
Cottonwood WWTP	CA0081507	Mun. WWTP	U/S of Delta / Yolo Bypass	Sacra-mento			X	X	X	0.29	2002 average		Tertiary	4.1*	1.6	0.096		0.038
Crystal Creek Aggregate	CA0082767	Aggregate	U/S of Delta / Yolo Bypass	Sacra-mento			X	X	X	0.002	average			4.8	0.013	0.010		2.8×10^{-5}
Davis WWTP Discharge 001	CA0079049	Mun. WWTP	U/S of Delta / Yolo Bypass	Yolo Bypass			X	X	X	2.8	WY2005	Secondary		7.4	17	0.550		1.3
Davis WWTP Discharge 002	CA0079049	Mun. WWTP	Delta/Yolo Bypass	Yolo Bypass			X	X	X	2.4	WY2005	Secondary		6.9	23	0.610		0.78
Defense Logistics Agency Sharpe GW Cleanup	CA0081931	WTP (GW)	U/S of Delta / Yolo Bypass	San Joaquin	X	Apr-08		X	X	1.9				2.6*	6.8	0.018		0.047
Deuel Vocational Institute WWTP	CA0078093	Mun. WWTP	Delta/Yolo Bypass	San Joaquin			X	X	X	0.47	WY2005	Tertiary		3.3	2.1	0.010		0.013
DFG Darrah Springs Fish Hatchery	CA0004561	Aqua-culture	U/S of Delta / Yolo Bypass	Sacra-mento			X			18.7	average					0.024		
DFG Feather River Fish Hatchery	CA0004570	Aqua-culture	U/S of Delta / Yolo Bypass	Sacra-mento			X			25.8	baseline			1.4				
DFG Merced River Fish Hatchery	CA0080055	Aqua-culture	U/S of Delta / Yolo Bypass	San Joaquin			X			4.55	average					0.037		
DFG Moccasin Creek Fish Hatchery	CA0004804	Aqua-culture	U/S of Delta / Yolo Bypass	San Joaquin			X			19.62	WY2005					0.010		

Table B.5: Summary of Facility Discharge Volumes and Effluent Total Mercury and Methylmercury Concentrations and Loads

Facility	NPDES No.	Facility Type	Proximity to Delta / Yolo Bypass [a]	Delta Subarea that Receives Discharge	NPDES Permit Rescinded During or After TMDL Study Period	NPDES Permit Rescinsion Date	Discharged in Sept. 2009 d/s Major Dams	Include in Sum of MeHg Source Loads d/s Major Dams for TMDL Period	Include in Sum of TotHg Source Loads d/s Major Dams for 20-yr Period	Annual Discharge (mgd)	Annual Discharge Type	Maximum Level of Mun. WWTP Treatment When EFF TotHg Data Were Collected	Treatment Category for Mun WWTPs d/s Major Dams w/o EFF TotHg Data	Ave. EFF TotHg Conc. [b] (ng/l)	EFF TotHg Load (g/yr)	Ave. EFF MeHg Conc. [b] (ng/l)	Treatment Category for EFF MeHg Conc. Estimate	EFF MeHg Load (g/yr)
DFG Mokelumne River Fish Hatchery	CA0004791	Aqua-culture	U/S of Delta / Yolo Bypass	Mokelumne			X			21	average					0.041		
DFG Nimbus Fish Hatchery	CA0004774	Aqua-culture	U/S of Delta / Yolo Bypass	Sacra-mento			X			40	baseline			26.8		0.065		
DFG San Joaquin Fish Hatchery	CA0004812	Aqua-culture	U/S of Delta / Yolo Bypass	San Joaquin			X			22.6	average					0.060		
DFG Thermalito Annex Fish Hatchery	CA0082350	Aqua-culture	U/S of Delta / Yolo Bypass	Sacra-mento			X			7.8	average			1.5				
DGS Office of State Publishing	CA0078875	Publishing	U/S of Delta / Yolo Bypass	Sacra-mento			X	X	X	0.3	WY2005			1.5	0.62	0.010		0.0041
Discovery Bay WWTP	CA0078590	Mun. WWTP	Delta/Yolo Bypass	Central			X	X	X	1.5	WY2005	Secondary		5.0	10	0.178		0.37
Donner Summit WWTP	CA0081621	Mun. WWTP	U/S of Major Dam	Sacra-mento								Tertiary		7.8				
El Dorado ID Deer Creek WWTP	CA0078662	Mun. WWTP	U/S of Delta / Yolo Bypass	Mokelumne			X	X	X	2.52	WY2005	Tertiary		5.1	18	0.015		0.052
El Dorado ID El Dorado Hills WWTP Discharge 1	CA0078671	Mun. WWTP	U/S of Delta / Yolo Bypass	Mokelumne			X	X	X	1.08	WY2005	Tertiary		2.0	3.0	0.018		0.027
Formica Corporation Sierra Plant	CA0004057	Manufactu ring	U/S of Delta / Yolo Bypass	Sacra-mento	X	Apr-09		X	X	0.88	average			3.5	4.3	0.050		0.061
Galt WWTP	CA0081434	Mun. WWTP	U/S of Delta / Yolo Bypass	Mokelumne			X	X	X	1.92	WY2005	Secondary		3.7	9.8	0.139		0.37
Gaylord Container Corp. Antioch Pulp and Paper Mill	CA0004847	Heating / Cooling	Delta/Yolo Bypass	West	X	Jun-06								7.1		0.055		
General Electric Co. GWCS	CA0081833	WTP (GW)	U/S of Delta / Yolo Bypass	San Joaquin			X	X	X	1.6	average			2.6*	5.7	0.010		0.022

Table B.5: Summary of Facility Discharge Volumes and Effluent Total Mercury and Methylmercury Concentrations and Loads

Facility	NPDES No.	Facility Type	Proximity to Delta / Yolo Bypass [a]	Delta Subarea that Receives Discharge	NPDES Permit Rescinded During or After TMDL Study Period	NPDES Permit Rescinsion Date	Discharged in Sept. 2009 d/s Major Dams	Include in Sum of MeHg Source Loads d/s Major Dams for TMDL Period	Include in Sum of TotHg Source Loads d/s Major Dams for 20-yr Period	Annual Discharge (mgd)	Annual Discharge Type	Maximum Level of Mun. WWTP Treatment When EFF TotHg Data Were Collected	Treatment Category for Mun WWTPs d/s Major Dams w/o EFF TotHg Data	Ave. EFF TotHg Conc. [b] (ng/l)	EFF TotHg Load (g/yr)	Ave. EFF MeHg Conc. [b] (ng/l)	Treatment Category for EFF MeHg Conc. Estimate	EFF MeHg Load (g/yr)
Grass Valley WWTP	CA0079898	Mun. WWTP	U/S of Major Dam	Sacra-mento						2.1	WY2005	Secondary		5.0		0.160		0.46
Grizzly Lake Resort Dellecker WWTP	CA0081744	Mun. WWTP	U/S of Major Dam	Sacra-mento								Secondary		8.6				
GWF Power Systems	CA0082309	Power	Delta/Yolo Bypass	West			X	X	X	0.05	WY2005			4.3	0.27	0.020		0.0019
Hershey Chocolate USA, Oakdale	CA0004146	Food	U/S of Delta / Yolo Bypass	San Joaquin			X	X	X	1.03	WY2005					0.010		0.014
J.F. Enterprises Worm Farm	CA0081949	Aqua-culture	U/S of Delta / Yolo Bypass	San Joaquin			X			5.44	maximum flow							
J.F. Shea CO Fawndale Rock and Asphalt	CA0083097	Aggregate	U/S of Delta / Yolo Bypass	Sacra-mento			X	X	X	3.87	average			4.8*	26	0.010		0.053
Jackson WWTP	CA0079391	Mun. WWTP	U/S of Major Dam	Mokelumne						0.56	WY2005	Tertiary		6.1		0.108		0.11
Kinder Morgan Elmira Remediation Project	CA0084719	WTP (GW)	U/S of Delta / Yolo Bypass	Yolo Bypass	X	Jun-08		X	X	0.07				2.6*	0.25	0.013		0.0013
Kinder Morgan Fox Rd Pipeline Release Site	CA0084760	WTP (GW)	U/S of Delta / Yolo Bypass	Yolo Bypass			X	X	X	0.072	average			2.6*	0.26	0.013		0.0013
Kinder Morgan Holt Ground Water Recovery	CA0084701	WTP (GW)	Delta/Yolo Bypass	Central	X	Jun-05		X	X	0.044	monthly average			2.5	0.15	0.013		0.00079
Land O'Lakes, Inc., Valley Gold LLC	CA0084808	Food	U/S of Delta / Yolo Bypass	San Joaquin			X	X	X	0.152	baseline					0.014*	Food	0.0029
Lehigh Southwest Cement Co.	CA0081191	Aggregate	U/S of Delta / Yolo Bypass	Sacra-mento			X	X	X		typically little discharge							

Table B.5: Summary of Facility Discharge Volumes and Effluent Total Mercury and Methylmercury Concentrations and Loads

Facility	NPDES No.	Facility Type	Proximity to Delta / Yolo Bypass [a]	Delta Subarea that Receives Discharge	NPDES Permit Rescinded During or After TMDL Study Period	NPDES Permit Rescinsion Date	Discharged in Sept. 2009 d/s Major Dams	Include in Sum of MeHg Source Loads d/s Major Dams for TMDL Period	Include in Sum of TotHg Source Loads d/s Major Dams for 20-yr Period	Annual Discharge (mgd)	Annual Discharge Type	Maximum Level of Mun. WWTP Treatment When EFF TotHg Data Were Collected	Treatment Category for Mun WWTPs d/s Major Dams w/o EFF TotHg Data	Ave. EFF TotHg Conc. [b] (ng/l)	EFF TotHg Load (g/yr)	Ave. EFF MeHg Conc. [b] (ng/l)	Treatment Category for EFF MeHg Conc. Estimate	EFF MeHg Load (g/yr)
Lincoln Center Groundwater Treatment Facility	CA0084255	WTP (GW)	Delta/Yolo Bypass	Central			X	X	X	0.25				0.6	0.21	0.03*	WTP (GW)	0.010
Lincoln WWTP	CA0084476	Mun. WWTP	U/S of Delta / Yolo Bypass	Sacra-mento			X	X	X	1.13	WY2005	Tertiary		1.4	2.2	0.018		0.028
Linda Co Water Dist WWTP	CA0079651	Mun. WWTP	U/S of Delta / Yolo Bypass	Sacra-mento			X	X	X	1.3	baseline	Secondary		20.7	37	0.018*	Mun WWTP: N/D + Filtration + Chlor./ Dechlor.	0.032
Live Oak WWTP	CA0079022	Mun. WWTP	U/S of Delta / Yolo Bypass	Sacra-mento			X	X	X	1.7	Nov04-Oct05		Secondary	8.7*	20	0.591		1.4
LLNL Site 300 GW Treatment	CA0082651	WTP (GW)	U/S of Delta / Yolo Bypass	San Joaquin	X	Aug-05			X	0.065	average			2.6*	0.23	0.013		
Lodi White Slough WWTP	CA0079243	Mun. WWTP	Delta/Yolo Bypass	Central			X	X	X	4.5	WY2005	Tertiary		3.3	21	0.128		0.93
Manteca WWTP	CA0081558	Mun. WWTP	Delta/Yolo Bypass	San Joaquin			X	X	X	4.63	WY2005	Secondary		10.6	68	0.216		1.4
Mariposa PUD WWTP	CA0079430	Mun. WWTP	U/S of Delta / Yolo Bypass	San Joaquin			X	X	X	0.245	average		Secondary	8.7*	2.9	0.393		0.13
Maxwell PUD WWTP	CA0079987	Mun. WWTP	U/S of Delta / Yolo Bypass	Sacra-mento			X	X	X	0.14	average		Secondary	8.7*	1.7	0.993		0.19
Merced WWTP	CA0079219	Mun. WWTP	U/S of Delta / Yolo Bypass	San Joaquin			X	X	X	8.5	baseline	Secondary		9.3	109	0.386		4.5
Metropolitan Stevedore	CA0084174	Port Terminal	Delta/Yolo Bypass	Central			X	X	X		(g)							
Mirant Delta LLC Contra Costa Power Plant, Outfall 1	CA0004863	Power	Delta/Yolo Bypass	West			X			2.9	WY2005			6.1		0.075		

Table B.5: Summary of Facility Discharge Volumes and Effluent Total Mercury and Methylmercury Concentrations and Loads

Facility	NPDES No.	Facility Type	Proximity to Delta / Yolo Bypass [a]	Delta Subarea that Receives Discharge	NPDES Permit Rescinded During or After TMDL Study Period	NPDES Permit Rescinsion Date	Discharged in Sept. 2009 d/s Major Dams	Include in Sum of MeHg Source Loads d/s Major Dams for TMDL Period	Include in Sum of TotHg Source Loads d/s Major Dams for 20-yr Period	Annual Discharge (mgd)	Annual Discharge Type	Maximum Level of Mun. WWTP Treatment When EFF TotHg Data Were Collected	Treatment Category for Mun WWTPs d/s Major Dams w/o EFF TotHg Data	Ave. EFF TotHg Conc. [b] (ng/l)	EFF TotHg Load (g/yr)	Ave. EFF MeHg Conc. [b] (ng/l)	Treatment Category for EFF MeHg Conc. Estimate	EFF MeHg Load (g/yr)
Mirant Delta LLC Contra Costa Power Plant, Outfall 2	CA0004863	Power	Delta/Yolo Bypass	West			X			121.0	WY2005			7.1		0.086		
Modesto ID Regional WTP	CA0083801	Water Filtration	U/S of Delta / Yolo Bypass	San Joaquin	X	Sep-07		X	X	0.04	WY2005			4.6*	0.25	0.056		0.0031
Modesto WWTP	CA0079103	Mun. WWTP	U/S of Delta / Yolo Bypass	San Joaquin			X	X	X	11.8	WY2005	Secondary		5.7	93	0.130		2.1
Mountain House CSD WWTP	CA0084271	Mun. WWTP	Delta/Yolo Bypass	San Joaquin			X			0.45	(h)	Tertiary	Tertiary	0.8	0.50	0.050		0.031
Mt Lassen Trout Farms Dales Facility	CA0080381	Aqua-culture	U/S of Delta / Yolo Bypass	Sacra-mento			X			2.4	average							
Mt Lassen Trout Farms Jeffcoat Facility	CA0082104	Aqua-culture	U/S of Delta / Yolo Bypass	Sacra-mento			X			2	baseline							
Mt Lassen Trout Farms Jeffcoat West Facility	CA0082813	Aqua-culture	U/S of Delta / Yolo Bypass	Sacra-mento			X			4.5	average							
Mt Lassen Trout Farms Meadowbrook Facility	CA0080373	Aqua-culture	U/S of Delta / Yolo Bypass	Sacra-mento			X			2.76	average							
Mt Lassen Trout Farms Millseat Facility	CA0082279	Aqua-culture	U/S of Delta / Yolo Bypass	Sacra-mento			X			14	average							
Mt Lassen Trout Farms Volta Facility	CA0083879	Aqua-culture	U/S of Delta / Yolo Bypass	Sacra-mento			X			1.9	average							
Mt Lassen Trout Farms Willow Springs Facility	CA0082163	Aqua-culture	U/S of Delta / Yolo Bypass	Sacra-mento			X			3	average							
Nevada City WWTP	CA0079901	Mun. WWTP	U/S of Major Dam	Sacra-mento						0.43	average			7.1		0.048		0.029

Table B.5: Summary of Facility Discharge Volumes and Effluent Total Mercury and Methylmercury Concentrations and Loads

Facility	NPDES No.	Facility Type	Proximity to Delta / Yolo Bypass [a]	Delta Subarea that Receives Discharge	NPDES Permit Rescinded During or After TMDL Study Period	NPDES Permit Rescission Date	Discharged in Sept. 2009 d/s Major Dams	Include in Sum of MeHg Source Loads d/s Major Dams for TMDL Period	Include in Sum of TotHg Source Loads d/s Major Dams for 20-yr Period	Annual Discharge (mgd)	Annual Discharge Type	Maximum Level of Mun. WWTP Treatment When EFF TotHg Data Were Collected	Treatment Category for Mun WWTPs d/s Major Dams w/o EFF TotHg Data	Ave. EFF TotHg Conc. [b] (ng/l)	EFF TotHg Load (g/yr)	Ave. EFF MeHg Conc. [b] (ng/l)	Treatment Category for EFF MeHg Conc. Estimate	EFF MeHg Load (g/yr)
Nevada Co SD #1 Cascade Shores WWTP	CA0083241	Mun. WWTP	U/S of Major Dam	Sacra-mento						0.026	average					0.142		0.0051
Nevada Co SD #1 Lake Wildwood WWTP	CA0077828	Mun. WWTP	U/S of Major Dam	Sacra-mento						0.5	1999-2002 annual average					0.109		0.075
Nevada Co SD #2 Lake of the Pines WWTP	CA0081612	Mun. WWTP	U/S of Major Dam	Sacra-mento						0.54	baseline					1.409		1.1
Oakwood Lake Subdivision Mining Reclamation	CA0082783	Lake Dewatering	Delta/Yolo Bypass	San Joaquin			X	X	X	9.15	WY2005			2.9	37	0.030		0.38
Olivehurst PUD WWTP	CA0077836	Mun. WWTP	U/S of Delta / Yolo Bypass	Sacra-mento			X	X	X	1.2	WY2005		Secondary	8.7*	22	0.144		0.24
Oroville WWTP	CA0079235	Mun. WWTP	U/S of Delta / Yolo Bypass	Sacra-mento			X	X	X	3	average	Tertiary		3.7	15	0.147		0.61
Pacific Coast Sprout Farms, Inc. (Sacramento Facility)	CA0082961	Aqua-culture	U/S of Delta / Yolo Bypass	Sacra-mento			X			0.1	baseline			1.8		0.010		
Pactiv Molded Pulp Mill	CA0004821	Paper Mill / Saw Mills	U/S of Delta / Yolo Bypass	Sacra-mento			X	X	X	1.9	average			2.0	5.3	0.039		0.10
Paradise Irrigation District	CA0083488	Water Filtration	U/S of Major Dam	Sacra-mento						1.5	design flow			4.7	9.7	0.013		
Placer Co. SA #28 Zone #6 WWTP	CA0079341	Mun. WWTP	U/S of Delta / Yolo Bypass	Sacra-mento			X	X	X	0.01	WY2005	Secondary		9.3	0.13	0.668		0.0092
Placer Co. SMD #1 WWTP	CA0079316	Mun. WWTP	U/S of Delta / Yolo Bypass	Sacra-mento			X	X	X	1.90	WY2005	Tertiary		2.1	5.7	0.141		0.37
Placer Co. SMD #3 WWTP	CA0079367	Mun. WWTP	U/S of Delta / Yolo Bypass	Sacra-mento			X	X	X	0.12	WY2005	Tertiary		2.1	0.35	0.100		0.017
Placerville Hangtown Creek WWTP	CA0078956	Mun. WWTP	U/S of Major Dam	Sacra-mento						1.3	average	Tertiary		11.6		0.058		0.10

Table B.5: Summary of Facility Discharge Volumes and Effluent Total Mercury and Methylmercury Concentrations and Loads

Facility	NPDES No.	Facility Type	Proximity to Delta / Yolo Bypass [a]	Delta Subarea that Receives Discharge	NPDES Permit Rescinded During or After TMDL Study Period	NPDES Permit Rescinsion Date	Discharged in Sept. 2009 d/s Major Dams	Include in Sum of MeHg Source Loads d/s Major Dams for TMDL Period	Include in Sum of TotHg Source Loads d/s Major Dams for 20-yr Period	Annual Discharge (mgd)	Annual Discharge Type	Maximum Level of Mun. WWTP Treatment When EFF TotHg Data Were Collected	Treatment Category for Mun WWTPs d/s Major Dams w/o EFF TotHg Data	Ave. EFF TotHg Conc. [b] (ng/l)	EFF TotHg Load (g/yr)	Ave. EFF MeHg Conc. [b] (ng/l)	Treatment Category for EFF MeHg Conc. Estimate	EFF MeHg Load (g/yr)
Planada Comm. Service Dist. WWTP	CA0078950	Mun. WWTP	U/S of Delta / Yolo Bypass	San Joaquin			X	X	X	0.38	average		Tertiary	4.1*	2.2	1.168		0.61
Pliant Corp Vitafilm Plant	CA0080071	Heating / Cooling	U/S of Delta / Yolo Bypass	San Joaquin	X	Dec-06				0.338								
Portola WWTP	CA0077844	Mun. WWTP	U/S of Major Dam	Sacra-mento								Secondary		4.9				
Proctor & Gamble Co. WWTP	CA0004316	Manufactu ring	U/S of Delta / Yolo Bypass	Sacra-mento	X	Jun-06		X	X	5.5				1.9	14	0.010		0.076
Quincy WWTP	CA0078981	Mun. WWTP	U/S of Major Dam	Sacra-mento								Secondary		15.8				
Red Bluff WWTP	CA0078891	Mun. WWTP	U/S of Delta / Yolo Bypass	Sacra-mento			X	X	X	1.4	baseline		Tertiary	4.1*	7.9	0.027		0.052
Redding Clear Creek WWTP	CA0079731	Mun. WWTP	U/S of Delta / Yolo Bypass	Sacra-mento			X	X	X	7.5	baseline	Tertiary		3.7	38	0.042		0.44
Redding Stillwater WWTP	CA0082589	Mun. WWTP	U/S of Delta / Yolo Bypass	Sacra-mento			X	X	X	3.46	WY2000-02 average	Tertiary		2.1	10	0.013		0.062
Rio Alto WD- Lake CA WWTP	CA0077852	Mun. WWTP	U/S of Delta / Yolo Bypass	Sacra-mento			X	X	X	0.15	dry weather average		Tertiary	4.1*	0.85	1.746		0.36
Rio Vista Northwest WWTP	CA0083771	Mun. WWTP	Delta/Yolo Bypass	Sacra-mento			X			1	(i)		Tertiary	4.1*	5.7	0.05*	Mun WWTP: N/D + Filtration + UV	0.069
Rio Vista Trilogy WWTP	CA0083771	Mun. WWTP	Delta/Yolo Bypass	Sacra-mento	X	Replaced by Rio Vista Northwest WWTP in 2007.		X	X	0.1	seasonal discharge (181 days)	Secondary		3.7	0.52	0.06*	Mun WWTP: Filtration + Chlor./ Dechlor. + Activated Sludge + Trickling Filter	0.0041

Table B.5: Summary of Facility Discharge Volumes and Effluent Total Mercury and Methylmercury Concentrations and Loads

Facility	NPDES No.	Facility Type	Proximity to Delta / Yolo Bypass [a]	Delta Subarea that Receives Discharge	NPDES Permit Rescinded During or After TMDL Study Period	NPDES Permit Rescinsion Date	Discharged in Sept. 2009 d/s Major Dams	Include in Sum of MeHg Source Loads d/s Major Dams for TMDL Period	Include in Sum of TotHg Source Loads d/s Major Dams for 20-yr Period	Annual Discharge (mgd)	Annual Discharge Type	Maximum Level of Mun. WWTP Treatment When EFF TotHg Data Were Collected	Treatment Category for Mun WWTPs d/s Major Dams w/o EFF TotHg Data	Ave. EFF TotHg Conc. [b] (ng/l)	EFF TotHg Load (g/yr)	Ave. EFF MeHg Conc. [b] (ng/l)	Treatment Category for EFF MeHg Conc. Estimate	EFF MeHg Load (g/yr)
Rio Vista WWTP	CA0079588	Mun. WWTP	Delta/Yolo Bypass	Sacra-mento			X	X	X	0.47	WY2005	Secondary		9.5	6.2	0.164		0.10
River Highlands CSD Hammonton Gold Village WWTP	CA0081574	Mun. WWTP	U/S of Delta / Yolo Bypass	Sacra-mento			X	X	X	0.008	baseline	Secondary		6.9	0.076	0.902*	Mun WWTP: Pond + Chlor./ Dechlor.	0.010
Roseville Dry Creek WWTP	CA0079502	Mun. WWTP	U/S of Delta / Yolo Bypass	Sacra-mento			X	X	X	10.19	WY2005	Tertiary		10.9	196	0.023		0.41
Roseville Pleasant Grove WWTP	CA0084573	Mun. WWTP	U/S of Delta / Yolo Bypass	Sacra-mento			X			5.90	WY2005 (j)	Tertiary		1.3	8.7	0.017		0.11
Sacramento Cogen Authority Procter & Gamble Plant	CA0083569	Power	U/S of Delta / Yolo Bypass	Sacra-mento	X	Sep-06				1.5				5.5		0.052		
Sacramento Combined WWTP (CWTP)	CA0079111	Combined Mun. WWTP	Delta/Yolo Bypass	Sacra-mento			X	X	X	0.59		Primary		66	54	0.536		0.44
Sacramento Combined WWTP (Pioneer)	CA0079111	Combined Mun. WWTP	Delta/Yolo Bypass	Sacra-mento			X	X	X	0.27				104	60	0.536		0.20
Sacramento Combined WWTP (Sump 2)	CA0079111	Combined Mun. WWTP	Delta/Yolo Bypass	Sacra-mento			X	X	X	0.42				101	38	0.536		0.31
Sacramento International Airport	CA0034841	Heating / Cooling	U/S of Delta / Yolo Bypass	Sacra-mento	X	Jun-06				1.5	design flow					0.035		
Sacramento Power Authority Campbells Cogen Plant	CA0083658	Power	U/S of Delta / Yolo Bypass	Sacra-mento	X	Mar-05								18.8				
San Andreas SD WWTP	CA0079464	Mun. WWTP	U/S of Major Dam	Central						0.3	baseline					0.249		0.10

Table B.5: Summary of Facility Discharge Volumes and Effluent Total Mercury and Methylmercury Concentrations and Loads

Facility	NPDES No.	Facility Type	Proximity to Delta / Yolo Bypass [a]	Delta Subarea that Receives Discharge	NPDES Permit Rescinded During or After TMDL Study Period	NPDES Permit Rescinsion Date	Discharged in Sept. 2009 d/s Major Dams	Include in Sum of MeHg Source Loads d/s Major Dams for TMDL Period	Include in Sum of TotHg Source Loads d/s Major Dams for 20-yr Period	Annual Discharge (mgd)	Annual Discharge Type	Maximum Level of Mun. WWTP Treatment When EFF TotHg Data Were Collected	Treatment Category for Mun WWTPs d/s Major Dams w/o EFF TotHg Data	Ave. EFF TotHg Conc. [b] (ng/l)	EFF TotHg Load (g/yr)	Ave. EFF MeHg Conc. [b] (ng/l)	Treatment Category for EFF MeHg Conc. Estimate	EFF MeHg Load (g/yr)
San Joaquin Co DPW CSA 31 Flag City WWTP	CA0082848	Mun. WWTP	Delta/Yolo Bypass	Central	X	Jun-08		X	X	0.06	WY2005	Tertiary		9.1	0.27	0.081		0.0066
Shasta Lake WTP	CA0004693	Water Filtration	U/S of Delta / Yolo Bypass	Sacra-mento			X	X	X	0.05	average			4.6*	0.32	0.025		0.0017
Shasta Lake WWTP	CA0079511	Mun. WWTP	U/S of Delta / Yolo Bypass	Sacra-mento			X	X	X	0.64	baseline		Tertiary	4.1*	3.6	0.022		0.019
Shasta Paper Co Shasta Mill	CA0004065	Paper Mill / Saw Mills	U/S of Delta / Yolo Bypass	Sacra-mento	X	Jan-05		X	X		(d)							
Sliger Mine	CA0084905	Mines	U/S of Major Dam	Sacra-mento						0.0646	average portal discharge					0.064		0.0057
SMUD Rancho Seco Nuclear Generating Station	CA0004758	Power/Domestic WWTP	U/S of Delta / Yolo Bypass	Mokelumne	X	Aug-09		X	X	0.09	average			0.8	0.10	0.040		0.0050
South Feather Water & Power Agency Miners Ranch WTP	CA0083143	Water Filtration	U/S of Delta / Yolo Bypass	Sacra-mento			X	X	X	0.25	baseline			4.6	1.6	0.013		0.0045
SPI Anderson Division	CA0082066	Paper Mill / Saw Mills	U/S of Delta / Yolo Bypass	Sacra-mento			X	X	X		typically no discharge					0.106		
SPI Camino Sawmill	CA0078841	Paper Mill / Saw Mills	U/S of Major Dam	Sacra-mento										3.3				
SPI Martell Complex/Sierra Pine	CA0004219	Paper Mill / Saw Mills	U/S of Delta / Yolo Bypass	Mokelumne			X	X	X	0.57	baseline			11.7	9.2	0.117*	Paper Mill /Saw Mills	0.092
SPI Quincy Division	CA0080357	Paper Mill / Saw Mills	U/S of Major Dam	Sacra-mento										6.2				
SPI Shasta Lake	CA0081400	Paper Mill / Saw Mills	U/S of Delta / Yolo Bypass	Sacra-mento			X	X	X	0.15	baseline			5.8*	1.4	0.117*	Paper Mill /Saw Mills	0.024
SRCSD Sacramento River WWTP	CA0077682	Mun. WWTP	Delta/Yolo Bypass	Sacra-mento			X	X	X	162	WY2001-2003	Secondary		7.3	1,634	0.718		161

Table B.5: Summary of Facility Discharge Volumes and Effluent Total Mercury and Methylmercury Concentrations and Loads

Facility	NPDES No.	Facility Type	Proximity to Delta / Yolo Bypass [a]	Delta Subarea that Receives Discharge	NPDES Permit Rescinded During or After TMDL Study Period	NPDES Permit Rescinsion Date	Discharged in Sept. 2009 d/s Major Dams	Include in Sum of MeHg Source Loads d/s Major Dams for TMDL Period	Include in Sum of TotHg Source Loads d/s Major Dams for 20-yr Period	Annual Discharge (mgd)	Annual Discharge Type	Maximum Level of Mun. WWTP Treatment When EFF TotHg Data Were Collected	Treatment Category for Mun WWTPs d/s Major Dams w/o EFF TotHg Data	Ave. EFF TotHg Conc. [b] (ng/l)	EFF TotHg Load (g/yr)	Ave. EFF MeHg Conc. [b] (ng/l)	Treatment Category for EFF MeHg Conc. Estimate	EFF MeHg Load (g/yr)
SRCSD Walnut Grove WWTP	CA0078794	Mun. WWTP	Delta/Yolo Bypass	Sacra-mento	X	(e)		X	X	0.08		Secondary		21.5	2.4	2.155		0.24
State of California Central Heating/Cooling Plant	CA0078581	Heating / Cooling	Delta/Yolo Bypass	Sacra-mento			X			5.26	WY2005			2.8		0.015		
Stimpel Wiebelhaus Assoc. SWA at Mountain Gate Quarry	CA0084140	Aggregate	U/S of Delta / Yolo Bypass	Sacra-mento			X	X	X	0.02	average			4.8*	0.13	0.081		0.0022
Stockton Congeneration Co.	CA0081965	Power	U/S of Delta / Yolo Bypass	San Joaquin	X	Oct-06				1.17				0.3		0.017		
Stockton WWTP	CA0079138	Mun. WWTP	Delta/Yolo Bypass	San Joaquin			X	X	X	28	WY2005	Tertiary		5.1	201	0.935		36
Tehama Co SD 1 Mineral WWTP	CA0084069	Mun. WWTP	U/S of Delta / Yolo Bypass	Sacra-mento			X	X	X	0.027	baseline		Tertiary	4.1*	0.15	1.04*	Mun WWTP: Pond + Filtration + Chlor./ Dechlor.	0.039
The Vendo Co GW Cleanup System	CA0083046	WTP (GW)	U/S of Delta / Yolo Bypass	San Joaquin			X	X	X	0.72	baseline			2.6*	2.6	0.013		0.013
Tracy WWTP	CA0079154	Mun. WWTP	Delta/Yolo Bypass	San Joaquin			X	X	X	9.49	WY2005	Secondary		11.0	145	0.145		1.8
Tuolumne UD Sonora WWTP/ Jamestown WWTP	CA0084727	Mun. WWTP	U/S of Major Dam	San Joaquin						0.16	WY2005					0.182		0.040
Turlock WWTP	CA0078948	Mun. WWTP	U/S of Delta / Yolo Bypass	San Joaquin			X	X	X	11.7	WY2005	Secondary		9.3	151	0.059		0.95
U.S. Army Corp of Engineers Titan 1-A Missile Facility	CA0084743	WTP (GW)	U/S of Delta / Yolo Bypass	Sacra-mento	X	Jun-07		X	X	0.0432				2.6*	0.16	0.013		0.00078

Table B.5: Summary of Facility Discharge Volumes and Effluent Total Mercury and Methylmercury Concentrations and Loads

Facility	NPDES No.	Facility Type	Proximity to Delta / Yolo Bypass [a]	Delta Subarea that Receives Discharge	NPDES Permit Rescinded During or After TMDL Study Period	NPDES Permit Rescinsion Date	Discharged in Sept. 2009 d/s Major Dams	Include in Sum of MeHg Source Loads d/s Major Dams for TMDL Period	Include in Sum of TotHg Source Loads d/s Major Dams for 20-yr Period	Annual Discharge (mgd)	Annual Discharge Type	Maximum Level of Mun. WWTP Treatment When EFF TotHg Data Were Collected	Treatment Category for Mun WWTPs d/s Major Dams w/o EFF TotHg Data	Ave. EFF TotHg Conc. [b] (ng/l)	EFF TotHg Load (g/yr)	Ave. EFF MeHg Conc. [b] (ng/l)	Treatment Category for EFF MeHg Conc. Estimate	EFF MeHg Load (g/yr)
UC Davis Center for Aquatic Biology & Aquaculture Aquatic Center	CA0083348	Aqua-culture	U/S of Delta / Yolo Bypass	Yolo Bypass			X			0.67	WY2005					0.030		
UC Davis Center for Aquatic Biology & Aquaculture Putah Creek Facility	CA0083348	Aqua-culture	U/S of Delta / Yolo Bypass	Yolo Bypass			X			0.14	WY2005					0.082		
UC Davis Hydraulics Laboratory	CA0084182	Laboratory	U/S of Delta / Yolo Bypass	Yolo Bypass			X	X	X	0.01	average					0.057		0.00079
UC Davis WWTP	CA0077895	Mun. WWTP	U/S of Delta / Yolo Bypass	Yolo Bypass			X	X	X	1.93	WY2005		Tertiary	4.1*	11	0.038		0.10
United Auburn Indian Community Casino WWTP	CA0084697	Mun. WWTP	U/S of Delta / Yolo Bypass	Sacra-mento			X	X	X	0.15	WY2005		Tertiary	4.1*	0.85	0.010		0.0021
USAF McClellan AFB GW Ext & Trt Sys	CA0081850	WTP (GW)	U/S of Delta / Yolo Bypass	Sacra-mento			X	X	X	2.12	average			2.6*	7.6	0.013		0.038
USDI BR Winter Run Rearing Facility	CA0084298	Aqua-culture	U/S of Major Dam	Sacra-mento												0.010		
USDI FWS Coleman Fish Hatchery	CA0004201	Aqua-culture	U/S of Delta / Yolo Bypass	Sacra-mento			X			40.08	average					0.030		
USDI UC Davis Aquatic Weed Laboratory	CA0083364	Laboratory	U/S of Delta / Yolo Bypass	Yolo Bypass			X	X	X	0.05	baseline					0.057*	Labor-atory	0.0039
Vacaville Easterly WWTP	CA0077691	Mun. WWTP	U/S of Delta / Yolo Bypass	Yolo Bypass			X	X	X	9.26	WY2005	Secondary		3.1	40	0.024		0.31
West Sacramento WWTP	CA0079171	Mun. WWTP	Delta/Yolo Bypass	Sacra-mento	X	Apr-08		X	X	5.6		Secondary		3.1	26	0.050		0.39

Table B.5: Summary of Facility Discharge Volumes and Effluent Total Mercury and Methylmercury Concentrations and Loads

Facility	NPDES No.	Facility Type	Proximity to Delta / Yolo Bypass [a]	Delta Subarea that Receives Discharge	NPDES Permit Rescinded During or After TMDL Study Period	NPDES Permit Rescinsion Date	Discharged in Sept. 2009 d/s Major Dams	Include in Sum of MeHg Source Loads d/s Major Dams for TMDL Period	Include in Sum of TotHg Source Loads d/s Major Dams for 20-yr Period	Annual Discharge (mgd)	Annual Discharge Type	Maximum Level of Mun. WWTP Treatment When EFF TotHg Data Were Collected	Treatment Category for Mun WWTPs d/s Major Dams w/o EFF TotHg Data	Ave. EFF TotHg Conc. [b] (ng/l)	EFF TotHg Load (g/yr)	Ave. EFF MeHg Conc. [b] (ng/l)	Treatment Category for EFF MeHg Conc. Estimate	EFF MeHg Load (g/yr)
Wheelabrator Shasta Energy Co.	CA0081957	Power	U/S of Delta / Yolo Bypass	Sacra-mento			X			0.02	average					0.104		
Williams WWTP	CA0077933	Mun. WWTP	U/S of Delta / Yolo Bypass	Sacra-mento			X	X	X	0.44	WY2005		Secondary	8.7*	3.6	1.553		0.94
Willows WWTP	CA0078034	Mun. WWTP	U/S of Delta / Yolo Bypass	Sacra-mento			X	X	X	1.22	average		Secondary	8.7*	15	0.105*	Mun WWTP: Filtration + Chlor./ Dechlor.	0.18
Woodland WWTP	CA0077950	Mun. WWTP	Delta/Yolo Bypass	Yolo Bypass			X	X	X	6.05	WY2005	Secondary		6.1	51	0.031		0.25
Yuba City WWTP	CA0079260	Mun. WWTP	U/S of Delta / Yolo Bypass	Sacra-mento			X	X	X	5.5	(f)	Secondary		9.1	69	0.295		2.2
Yuba CWD Forbestown WTP	CA0084824	Water Filtration	U/S of Delta / Yolo Bypass	Sacra-mento			X	X	X	0.07	design flow			0.6	0.058	0.033*	Water Filtration	0.0032

Footnotes for Table B.5:

(a) U/S: Upstream.

(b) An asterisk (*) indicates that effluent total mercury and/or methylmercury concentration date were not available for these facilities. Average effluent concentrations observed at similar facilities were used to estimate their effluent loads. The average concentrations shown in this table for non-municipal WWTPs for which effluent total mercury and/or methylmercury concentration data were not available are based on the average of average effluent concentrations observed at facilities within their respective facility categories. Average total mercury concentrations for municipal WWTPs with tertiary and secondary treatment processes for which effluent data were not available are based on the average of the average total mercury concentrations observed at tertiary and secondary municipal WWTPs, 4.1 and 8.7 ng/l, respectively. Average methylmercury concentrations for municipal WWTPs for which effluent data were not available are based on the average concentrations observed at municipal treatment plants with a similar suite of treatment processes, as shown in Tables 17, 23 and 26.

(c) Altamont Landfill and Resource discharge: average wet weather/dry weather design prior to 1999; there has been no discharge since 1999.

(d) Shasta Paper Co Shasta Mill discharge: stormwater discharges only; there has been no discharge of treated process and domestic wastewater from the treatment plant to Sacramento River since 31 August 2001.

(e) SRCSD Walnut Grove WWTP discharge: The WWTP no longer discharges; as of March 2010, the NPDES permit has not yet been rescinded.

(f) Yuba City WWTP discharge: average daily flow for dates effluent was sampled for methylmercury.

(g) Metropolitan Stevedore discharge: the facility's discharge volume was not specified by its permit.

(h) Mountain House CSD WWTP discharge: Phase 1 dry weather design capacity; the WWTP began to discharge to surface water in 2007.

(i) Rio Vista Northwest WWTP discharge: start-up capacity; the WWTP began to discharge to surface water in 2007.

(j) Roseville Pleasant Grove WWTP discharge: the WWTPbegan to discharge to surface water in June 2004.

APPENDIX C
SUMMARY OF NPDES FACILITY EFFLUENT, INFLUENT, AND RECEIVING WATER MATRIX SPIKES AND MATRIX SPIKE DUPLICATES

Table C.1: Summary of Matrix Spike and Matrix Spike Duplicate Recoveries and Relative Percent Differences

NPDES NUMBER	FACILITY	DATE	MATRIX [(a)]	MS % RECOVERY	MSD % RECOVERY	RPD
CA0083861	AEROJET INTERIM GROUND WTP	11/17/05	Effluent	99.1%	107.4%	8.0%
CA0083861	AEROJET INTERIM GROUND WTP	06/06/06	Effluent	90.3%	98.4%	8.6%
CA0004111	AEROJET SACRAMENTO FACILITY	03/18/05	Effluent	86.5%	97.6%	12.1%
CA0004847	ANTIOCH PULP & PAPER MILL	09/23/04	Effluent	106.8%	103.9%	2.8%
CA0004847	ANTIOCH PULP & PAPER MILL	10/14/04	Effluent	118.9%	114.9%	3.4%
CA0083721	BELL CARTER INDUSTRIAL WWTP	03/02/05	Effluent	119.4%	103.4%	14.4%
CA0083721	BELL CARTER INDUSTRIAL WWTP	12/15/04	Effluent	100.3%	92.1%	8.5%
CA0080799	BELLA VISTA WTP	09/21/04	Effluent	105.7%	107.6%	1.8%
CA0084891	BOEING COMPANY INTERIM GW TRT SYSTEM	08/17/04	Effluent	86.8%	85.6%	1.4%
CA0078581	CA CENTRAL HEATING/COOLING FAC	12/15/04	Effluent	103.0%	108.6%	5.3%
CA0078581	CA CENTRAL HEATING/COOLING FAC	03/07/05	Effluent	102.4%	95.3%	7.2%
CA0078581	CA CENTRAL HEATING/COOLING FAC	08/25/04	Effluent	114.4%	101.2%	12.2%
CA0078581	CA CENTRAL HEATING/COOLING FAC	06/06/05	Effluent	117.0%	103.0%	12.7%
CA0078875	CA STATE PRINTING & WAREHOUSES	08/30/04	Effluent	98.5%	86.5%	13.0%
CA0083968	CALAMCO - STOCKTON TERMINAL	07/11/05	Effluent	120.0%	117.9%	1.8%
CA0083968	CALAMCO - STOCKTON TERMINAL	08/04/05	Effluent	125.5%	119.6%	4.8%
CA0083968	CALAMCO - STOCKTON TERMINAL	08/26/04	Effluent	122.3%	107.4%	13.0%
CA0081752	CALAVERAS TROUT FARM, INC TROUT REARING FAC.	09/30/04	Effluent	103.0%	107.9%	4.6%
CA0083828	CLEAR CREEK WTP	12/09/04	Effluent	111.6%	105.3%	5.8%
CA0083828	CLEAR CREEK WTP	06/27/05	Effluent	91.0%	106.7%	15.9%
CA0082767	CRYSTAL CREEK AGGREGATE	01/04/05	Effluent	100.1%	112.5%	11.7%
CA0081931	DEFENSE LOGISTICS AGENCY GW CLEANUP	09/27/04	Effluent	115.6%	115.6%	0.0%
CA0004561	DFG DARRAH SPRINGS HATCHERY	09/15/04	Effluent	115.5%	105.6%	9.0%
CA0004561	DFG DARRAH SPRINGS HATCHERY	09/14/04	Effluent	96.2%	111.4%	14.6%

Table C.1: Summary of Matrix Spike and Matrix Spike Duplicate Recoveries and Relative Percent Differences

NPDES NUMBER	FACILITY	DATE	MATRIX [a]	MS % RECOVERY	MSD % RECOVERY	RPD
CA0080055	DFG MERCED RIVER FISH HATCHERY	05/26/05	Effluent	120.2%	117.3%	2.4%
CA0004804	DFG MOCCASIN FISH HATCHERY	08/24/04	Effluent	92.0%	86.5%	6.2%
CA0004812	DFG SAN JOAQUIN FISH HATCHERY	09/28/04	Effluent	109.7%	108.8%	0.8%
CA0083097	FAWNDALE ROCK & ASPHALT	10/20/04	Effluent	102.3%	100.9%	1.4%
CA0083097	FAWNDALE ROCK & ASPHALT	10/20/04	Effluent	99.6%	119.9%	18.5%
CA0081833	GENERAL ELECTRIC CO GWCS	01/24/05	Effluent	120.6%	119.1%	1.3%
CA0081833	GENERAL ELECTRIC CO GWCS	07/05/05	Effluent	111.8%	108.1%	3.4%
CA0081833	GENERAL ELECTRIC CO GWCS	10/08/04	Effluent	114.0%	122.4%	7.1%
CA0082309	GWF POWER SYSTEMS, SITE IV	02/03/05	Effluent	97.8%	96.4%	1.4%
CA0082309	GWF POWER SYSTEMS, SITE IV	08/11/04	Effluent	94.8%	92.5%	2.5%
CA0004146	HERSHEY CHOCOLATE USA, OAKDALE	10/12/04	Effluent	111.5%	109.2%	2.1%
CA0004146	HERSHEY CHOCOLATE USA, OAKDALE	02/07/05	Effluent	100.9%	91.9%	9.3%
CA0083551	KONOCTI HARBOR INN	10/13/04	Effluent	110.8%	100.1%	10.1%
CA0081191	LEHIGH SOUTHWEST CEMENT CO	12/08/04	Effluent	111.3%	111.1%	0.2%
CA0081191	LEHIGH SOUTHWEST CEMENT CO	10/19/04	Effluent	107.0%	116.5%	8.5%
CA0081191	LEHIGH SOUTHWEST CEMENT CO	10/19/04	Effluent	116.7%	100.9%	14.5%
CA0081191	LEHIGH SOUTHWEST CEMENT CO	12/08/04	Effluent	121.6%	97.9%	21.6%
CA0082082	LOS BANOS FOODS, INC	09/07/04	Effluent	103.7%	89.9%	14.3%
CA0082783	MANTECA AGGREGATE SAND PLANT [b]	08/26/04	Effluent	96.5%	92.0%	4.8%
CA0083143	MINERS RANCH WTP	09/09/04	Effluent	106.6%	97.7%	8.7%
CA0004863	MIRANT CCPP ANTIOCH	11/02/04	Effluent	115.3%	122.6%	6.1%
CA0004863	MIRANT CCPP ANTIOCH	11/02/04	Effluent	123.5%	106.3%	15.0%
CA0083801	MODESTO ID REGIONAL WTP	01/18/05	Effluent	113.6%	111.3%	2.0%
CA0083801	MODESTO ID REGIONAL WTP	10/08/04	Effluent	113.8%	108.1%	5.1%
CA0083801	MODESTO ID REGIONAL WTP	04/11/05	Effluent	104.2%	95.8%	8.4%
CA0004821	PACTIV MOLDED PULP MILL	04/06/05	Effluent	116.8%	117.1%	0.3%
CA0004821	PACTIV MOLDED PULP MILL	08/03/05	Effluent	88.8%	100.5%	12.4%
CA0004821	PACTIV MOLDED PULP MILL	09/16/04	Effluent	123.5%	86.6%	35.1%

Table C.1: Summary of Matrix Spike and Matrix Spike Duplicate Recoveries and Relative Percent Differences

NPDES NUMBER	FACILITY	DATE	MATRIX [a]	MS % RECOVERY	MSD % RECOVERY	RPD
CA0083488	PARADISE WTP	09/08/04	Effluent	96.1%	103.7%	7.6%
CA0004316	PROCTER & GAMBLE CO WWTP	08/30/04	Effluent	124.6%	108.9%	13.4%
CA0083569	PROCTOR & GAMBLE COGEN. PLANT	08/11/04	Effluent	94.4%	93.2%	1.3%
CA0083569	PROCTOR & GAMBLE COGEN. PLANT	08/11/04	Effluent	100.0%	97.5%	2.5%
CA0034841	SACRAMENTO INTERNATIONAL AIRPT	08/31/04	Effluent	116.3%	110.6%	5.0%
CA0034841	SACRAMENTO INTERNATIONAL AIRPT	05/20/05	Effluent	103.0%	118.1%	13.7%
CA0004693	SHASTA LAKE WTP	11/12/04	Effluent	107.8%	104.1%	3.5%
CA0004693	SHASTA LAKE WTP	08/23/04	Effluent	80.5%	103.0%	24.5%
CA0082066	SIERRA PACIFIC, ANDERSON DIV	01/26/05	Effluent	95.2%	91.7%	3.7%
CA0082066	SIERRA PACIFIC, ANDERSON DIV	12/26/04	Effluent	102.6%	107.0%	4.2%
CA0082066	SIERRA PACIFIC, ANDERSON DIV	12/26/04	Effluent	112.7%	117.7%	4.3%
CA0082066	SIERRA PACIFIC, ANDERSON DIV	01/26/05	Effluent	93.8%	86.7%	7.9%
CA0081400	SIERRA PACIFIC, SHASTA LAKE DV	03/23/05	Effluent	103.2%	100.1%	3.0%
CA0081400	SIERRA PACIFIC, SHASTA LAKE DV	12/30/04	Effluent	91.2%	86.1%	5.8%
CA0084905	SLIGER MINE	12/20/05	Effluent	92.4%	99.1%	7.0%
CA0081965	STOCKTON COGENERATION FACILITY	08/18/04	Effluent	104.3%	96.1%	8.2%
CA0084182	UC DAVIS HYDRAULICS LABORATORY	09/22/04	Effluent	113.4%	110.3%	2.8%
CA0083348	UCDAVIS AQUATIC CENTER/ANIMAL SCIENCE	11/05/04	Effluent	103.7%	100.0%	3.6%
CA0083348	UCDAVIS AQUATIC CENTER/ANIMAL SCIENCE	09/22/04	Effluent	118.8%	124.6%	4.8%
CA0083348	UCDAVIS AQUATIC CENTER/ANIMAL SCIENCE	09/22/04	Effluent	116.7%	126.3%	7.9%
CA0004201	USDI FWS COLEMAN FISH HATCHERY	11/24/04	Effluent	112.8%	108.4%	4.0%
CA0084298	USDI FWS WINTER RUN REARING FACILITY	10/28/04	Effluent	118.1%	116.7%	1.2%
CA0081957	WHEELABRATOR SHASTA ENERGY CO	10/07/04	Effluent	91.0%	91.0%	0.0%
CA0077704	ANDERSON WWTP	10/06/04	Effluent (Mun-WW)	120.2%	128.4%	6.6%
CA0079197	ATWATER WWTP	09/28/04	Effluent (Mun-WW)	102.70%	107.70%	4.8%
CA0079219	ATWATER WWTP	09/14/04	Effluent (Mun-WW)	106.80%	106.60%	0.2%
CA0077712	AUBURN WWTP	10/06/04	Effluent (Mun-WW)	115.4%	115.9%	0.4%
CA0077712	AUBURN WWTP	08/31/04	Effluent (Mun-WW)	120.7%	115.1%	4.7%

Table C.1: Summary of Matrix Spike and Matrix Spike Duplicate Recoveries and Relative Percent Differences

NPDES NUMBER	FACILITY	DATE	MATRIX [a]	MS % RECOVERY	MSD % RECOVERY	RPD
CA0077712	AUBURN WWTP	07/12/05	Effluent (Mun-WW)	96.2%	117.8%	20.2%
CA0078930	BIGGS WWTP	08/23/04	Effluent (Mun-WW)	55.5%	56.0%	0.9%
CA0082660	BRENTWOOD WWTP	12/06/04	Effluent (Mun-WW)	107.6%	107.2%	0.4%
CA0082660	BRENTWOOD WWTP	11/01/04	Effluent (Mun-WW)	117.9%	119.3%	1.2%
CA0082660	BRENTWOOD WWTP	03/07/05	Effluent (Mun-WW)	115.9%	118.1%	1.9%
CA0082660	BRENTWOOD WWTP	10/04/04	Effluent (Mun-WW)	108.8%	110.9%	1.9%
CA0082660	BRENTWOOD WWTP	09/08/04	Effluent (Mun-WW)	109.5%	116.7%	6.4%
CA0082660	BRENTWOOD WWTP	01/03/05	Effluent (Mun-WW)	107.4%	99.7%	7.4%
CA0082660	BRENTWOOD WWTP	08/09/04	Effluent (Mun-WW)	99.4%	73.5%	30.0%
CA0079081	CHICO REGIONAL WWTP	05/10/05	Effluent (Mun-WW)	107.60%	107.60%	0.0%
CA0079081	CHICO REGIONAL WWTP	09/07/04	Effluent (Mun-WW)	106.10%	107.50%	1.3%
CA0079081	CHICO REGIONAL WWTP	06/14/05	Effluent (Mun-WW)	89.40%	91.70%	2.5%
CA0079731	CLEAR CREEK WWTP	06/09/05	Effluent (Mun-WW)	95.5%	95.5%	0.0%
CA0079731	CLEAR CREEK WWTP	09/08/04	Effluent (Mun-WW)	108.5%	105.5%	2.8%
CA0079529	COLFAX WWTP	11/10/04	Effluent (Mun-WW)	122.1%	117.0%	4.3%
CA0078999	COLUSA WWTP	08/26/04	Effluent (Mun-WW)	133.2%	91.9%	13.3%
CA0078999	COLUSA WWTP	12/02/04	Effluent (Mun-WW)	89.5%	90.7%	0.3%
CA0004995	CORNING INDUST/DOMESTIC WWTP	09/22/04	Effluent (Mun-WW)	122.3%	107.4%	13.0%
CA0081507	COTTONWOOD WWTP	09/30/04	Effluent (Mun-WW)	101.0%	106.8%	5.6%
CA0081507	COTTONWOOD WWTP	04/01/05	Effluent (Mun-WW)	98.7%	84.6%	15.4%
CA0079049	DAVIS WWTP	09/22/04	Effluent (Mun-WW)	102%	96%	6.1%
CA0078662	DEER CREEK WWTP	12/07/04	Effluent (Mun-WW)	92.5%	91.1%	1.5%
CA0078662	DEER CREEK WWTP	02/08/05	Effluent (Mun-WW)	105.5%	103.8%	1.6%
CA0078093	DEUEL VOCATNL INST. WWTP	04/20/05	Effluent (Mun-WW)	91.3%	92.5%	1.3%
CA0078093	DEUEL VOCATNL INST. WWTP	01/12/05	Effluent (Mun-WW)	99.5%	101.2%	1.7%
CA0078093	DEUEL VOCATNL INST. WWTP	10/26/04	Effluent (Mun-WW)	97.4%	93.8%	3.8%
CA0078590	DISCOVERY BAY WWTP	04/25/05	Effluent (Mun-WW)	87.9%	86.7%	1.4%
CA0078590	DISCOVERY BAY WWTP	08/18/04	Effluent (Mun-WW)	96.1%	92.0%	4.4%

Table C.1: Summary of Matrix Spike and Matrix Spike Duplicate Recoveries and Relative Percent Differences

NPDES NUMBER	FACILITY	DATE	MATRIX [a]	MS % RECOVERY	MSD % RECOVERY	RPD
CA0077691	EASTERLY WWTP	01/11/05	Effluent (Mun-WW)	87.1%	92.9%	6.4%
CA0078671	EL DORADO HILLS WWTP	06/07/05	Effluent (Mun-WW)	90.0%	90.0%	0.0%
CA0078671	EL DORADO HILLS WWTP	05/03/05	Effluent (Mun-WW)	95.3%	100.7%	5.5%
CA0078671	EL DORADO HILLS WWTP	01/04/05	Effluent (Mun-WW)	87.1%	92.3%	5.8%
CA0083682	FRENCH CAMP GOLF & RV PARK WWTP	08/17/04	Effluent (Mun-WW)	96.7%	98.0%	1.3%
CA0081434	GALT WWTP	11/02/04	Effluent (Mun-WW)	99.8%	117.0%	15.9%
CA0079898	GRASS VALLEY WWTP	06/02/05	Effluent (Mun-WW)	107.8%	105.6%	2.1%
CA0079898	GRASS VALLEY WWTP	08/26/04	Effluent (Mun-WW)	118.4%	109.3%	8.0%
CA0078956	HANGTOWN CREEK WWTP	07/27/05	Effluent (Mun-WW)	91.9%	93.8%	2.0%
CA0078956	HANGTOWN CREEK WWTP	08/18/04	Effluent (Mun-WW)	92.6%	107.7%	15.1%
CA0079391	JACKSON WWTP	09/14/04	Effluent (Mun-WW)	111.5%	112.3%	0.7%
CA0077852	LAKE CALIFORNIA WWTP	03/15/05	Effluent (Mun-WW)	102.1%	110.8%	8.2%
CA0081612	LAKE OF THE PINES WWTP	11/04/04	Effluent (Mun-WW)	97.4%	93.8%	3.8%
CA0077828	LAKE WILDWOOD WWTP	08/30/04	Effluent (Mun-WW)	106.0%	106.0%	0.0%
CA0077828	LAKE WILDWOOD WWTP	05/18/05	Effluent (Mun-WW)	100.0%	97.6%	2.4%
CA0084476	LINCOLN WWTP	10/20/05	Effluent (Mun-WW)	106.4%	106.5%	0.1%
CA0084476	LINCOLN WWTP	02/08/05	Effluent (Mun-WW)	103.8%	107.0%	3.0%
CA0079430	MARIPOSA WWTP	09/22/04	Effluent (Mun-WW)	106.0%	108.3%	2.4%
CA0079987	MAXWELL PUD WWTP	08/26/04	Effluent (Mun-WW)	79.8%	69.2%	14.2%
CA0079901	NEVADA CITY WWTP	08/30/04	Effluent (Mun-WW)	91.5%	104.0%	12.8%
CA0077836	OLIVEHURST WWTP	12/13/04	Effluent (Mun-WW)	80.7%	92.2%	13.3%
CA0077836	OLIVEHURST WWTP	08/23/04	Effluent (Mun-WW)	103.8%	89.3%	15.0%
CA0079235	OROVILLE WWTP	09/13/04	Effluent (Mun-WW)	97.70%	102.60%	4.9%
CA0079235	OROVILLE WWTP	10/18/04	Effluent (Mun-WW)	91.90%	99.70%	8.1%
CA0079316	PLACER CO SMD NO 1	09/01/04	Effluent (Mun-WW)	108.0%	103.7%	4.1%
CA0079316	PLACER CO SMD NO 1	10/06/04	Effluent (Mun-WW)	103.3%	96.5%	6.8%
CA0079367	PLACER CO SMD NO 3	08/25/04	Effluent (Mun-WW)	90.5%	87.8%	3.0%
CA0079367	PLACER CO SMD NO 3	09/01/04	Effluent (Mun-WW)	101.9%	108.9%	6.6%

Table C.1: Summary of Matrix Spike and Matrix Spike Duplicate Recoveries and Relative Percent Differences

NPDES NUMBER	FACILITY	DATE	MATRIX [a]	MS % RECOVERY	MSD % RECOVERY	RPD
CA0078950	PLANANDA CSD WWTP	12/13/04	Effluent (Mun-WW)	99.0%	107.0%	7.8%
CA0078891	RED BLUFF WWTP	02/09/05	Effluent (Mun-WW)	97.6%	97.9%	0.3%
CA0078891	RED BLUFF WWTP	09/16/04	Effluent (Mun-WW)	116.2%	113.1%	2.7%
CA0079588	RIO VISTA WWTP	04/25/05	Effluent (Mun-WW)	87.9%	86.7%	1.4%
CA0079588	RIO VISTA WWTP	08/18/04	Effluent (Mun-WW)	136.6%	109.1%	22.4%
CA0079464	SAN ANDREAS WWTP	12/29/04	Effluent (Mun-WW)	103.5%	101.9%	1.6%
CA0082848	SAN JOAQUIN CO DPW - FLAG CITY WWTP	04/21/05	Effluent (Mun-WW)	87.9%	86.7%	1.4%
CA0079511	SHASTA LAKE WWTP	11/12/04	Effluent (Mun-WW)	119.1%	111.3%	6.8%
CA0004758	SMUD RANCHO SECO NUCLEAR GEN STA 1	08/04/04	Effluent (Mun-WW)	93.6%	89.9%	4.0%
CA0082589	STILLWATER WWTP	06/09/05	Effluent (Mun-WW)	95.5%	95.5%	0.0%
CA0082589	STILLWATER WWTP	09/08/04	Effluent (Mun-WW)	129.8%	117.7%	9.8%
CA0079138	STOCKTON WWTP	11/10/04	Effluent (Mun-WW)	120.50%	120.10%	0.3%
CA0079138	STOCKTON WWTP	08/18/04	Effluent (Mun-WW)	99.70%	95.10%	4.7%
CA0079154	TRACY WWTP	10/06/04	Effluent (Mun-WW)	108.30%	106.90%	1.3%
CA0079154	TRACY WWTP	08/19/04	Effluent (Mun-WW)	48.30%	49.60%	2.7%
CA0079154	TRACY WWTP	06/22/05	Effluent (Mun-WW)	109.90%	115.40%	4.9%
CA0079154	TRACY WWTP	07/13/05	Effluent (Mun-WW)	90.70%	75.20%	18.7%
CA0078948	TURLOCK WWTP	08/23/04	Effluent (Mun-WW)	74.5%	75.5%	1.3%
CA0078794	WALNUT GROVE WWTP	04/06/05	Effluent (Mun-WW)	102.5%	110.0%	7.1%
CA0077933	WILLIAMS WWTP	08/25/04	Effluent (Mun-WW)	82.0%	122.0%	39.2%
CA0077950	WOODLAND WWTP	03/07/05	Effluent (Mun-WW)	104.1%	98.7%	5.3%
CA0077950	WOODLAND WWTP	08/11/04	Effluent (Mun-WW)	86.8%	100.5%	14.6%
CA0079260	YUBA CITY WWTP	08/24/04	Effluent (Mun-WW)	101.8%	111.7%	7.5%
CA0079260	YUBA CITY WWTP	11/22/04	Effluent (Mun-WW)	98.70%	97.40%	1.3%
CA0079260	YUBA CITY WWTP	05/26/05	Effluent (Mun-WW)	106.50%	93.90%	12.6%
CA0083968	CALAMCO - STOCKTON TERMINAL	08/26/04	Influent	102.6%	104.0%	1.4%
CA0081752	CALAVERAS TROUT FARM, INC TROUT REARING FAC.	09/30/04	Influent	113.6%	106.3%	6.6%
CA0004561	DFG DARRAH SPRINGS HATCHERY	09/15/04	Influent	100.5%	102.9%	2.4%

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NPDES NUMBER	FACILITY	DATE	MATRIX [a]	MS % RECOVERY	MSD % RECOVERY	RPD
CA0004561	DFG DARRAH SPRINGS HATCHERY	09/14/04	Influent	111.9%	114.9%	2.6%
CA0004812	DFG SAN JOAQUIN FISH HATCHERY	09/28/04	Influent	108.8%	111.9%	2.8%
CA0082309	GWF POWER SYSTEMS, SITE IV	05/05/05	Influent	99.6%	93.4%	6.4%
CA0004316	PROCTER & GAMBLE CO WWTP	11/01/04	Influent	108.6%	106.6%	1.9%
CA0004316	PROCTER & GAMBLE CO WWTP	02/16/05	Influent	94.2%	99.3%	5.3%
CA0079197	ATWATER WWTP	09/28/04	Influent (Mun-WW)	37.90%	53.10%	33.4%
CA0079081	CHICO REGIONAL WWTP	09/07/04	Influent (Mun-WW)	113.80%	106.10%	7.0%
CA0078999	COLUSA WWTP	08/26/04	Influent (Mun-WW)	39.8%	33.6%	5.3%
CA0078662	DEER CREEK WWTP	08/02/05	Influent (Mun-WW)	125.0%	118.6%	5.3%
CA0079898	GRASS VALLEY WWTP	05/05/05	Influent (Mun-WW)	108.8%	115.0%	5.5%
CA0079898	GRASS VALLEY WWTP	12/02/04	Influent (Mun-WW)	129.5%	101.3%	24.4%
CA0079898	GRASS VALLEY WWTP	08/26/04	Influent (Mun-WW)	63.5%	44.9%	34.3%
CA0079430	MARIPOSA WWTP	09/22/04	Influent (Mun-WW)	104.2%	104.8%	0.0%
CA0079987	MAXWELL PUD WWTP	08/26/04	Influent (Mun-WW)	87.0%	98.5%	12.4%
CA0079901	NEVADA CITY WWTP	08/30/04	Influent (Mun-WW)	44.6%	31.7%	33.8%
CA0079901	NEVADA CITY WWTP	06/02/05	Influent (Mun-WW)	113.2%	79.6%	34.9%
CA0079588	RIO VISTA WWTP	08/18/04	Influent (Mun-WW)	94.5%	90.7%	4.1%
CA0077933	WILLIAMS WWTP	08/25/04	Influent (Mun-WW)	33.4%	23.2%	36.0%
CA0077933	WILLIAMS WWTP	03/01/05	Influent (Mun-WW)	132.9%	84.2%	44.9%
CA0077950	WOODLAND WWTP	02/09/05	Influent (Mun-WW)	98.2%	95.7%	2.6%
CA0077950	WOODLAND WWTP	09/20/04	Influent (Mun-WW)	83.4%	85.7%	2.7%
CA0077950	WOODLAND WWTP	10/14/04	Influent (Mun-WW)	92.0%	99.8%	8.1%
CA0079197	ATWATER WWTP	09/28/04	Receiving Water	109.70%	107.10%	2.4%
CA0083721	BELL CARTER INDUSTRIAL WWTP	12/15/04	Receiving Water	116.4%	116.3%	0.1%
CA0083721	BELL CARTER INDUSTRIAL WWTP	03/02/05	Receiving Water	129.1%	133.3%	3.2%
CA0079081	CHICO REGIONAL WWTP	09/07/04	Receiving Water	95.60%	102.50%	7.0%
CA0079081	CHICO REGIONAL WWTP	01/18/05	Receiving Water	89.70%	98.20%	9.0%
CA0077691	EASTERLY WWTP	05/10/05	Receiving Water	109.0%	107.0%	1.9%

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NPDES NUMBER	FACILITY	DATE	MATRIX [a]	MS % RECOVERY	MSD % RECOVERY	RPD
CA0077691	EASTERLY WWTP	12/09/04	Receiving Water	105.0%	109.0%	3.7%
CA0077691	EASTERLY WWTP	01/11/05	Receiving Water	94.9%	88.5%	7.0%
CA0077691	EASTERLY WWTP	12/07/04	Receiving Water	97.2%	108.5%	11.0%
CA0004146	HERSHEY CHOCOLATE USA, OAKDALE	10/12/04	Receiving Water	105.5%	111.9%	5.9%
CA0081191	LEHIGH SOUTHWEST CEMENT CO	12/08/04	Receiving Water	114.0%	116.3%	2.0%
CA0081191	LEHIGH SOUTHWEST CEMENT CO	10/19/04	Receiving Water	105.5%	111.9%	5.9%
CA0081191	LEHIGH SOUTHWEST CEMENT CO	10/19/04	Receiving Water	117.5%	103.8%	12.4%
CA0079430	MARIPOSA WWTP	09/22/04	Receiving Water	110.3%	114.3%	3.4%
CA0079901	NEVADA CITY WWTP	08/30/04	Receiving Water	85.5%	83.5%	2.4%
CA0004821	PACTIV MOLDED PULP MILL	05/04/05	Receiving Water	118.0%	116.8%	1.0%
CA0004821	PACTIV MOLDED PULP MILL	09/16/04	Receiving Water	110.6%	116.8%	5.5%
CA0079316	PLACER CO SMD NO 1	08/05/04	Receiving Water	97.8%	106.1%	8.1%
CA0083569	PROCTOR & GAMBLE COGEN. PLANT	08/11/04	Receiving Water	98.8%	95.1%	3.8%
CA0081400	SIERRA PACIFIC, SHASTA LAKE DV	03/23/05	Receiving Water	100.0%	99.6%	0.4%
CA0081400	SIERRA PACIFIC, SHASTA LAKE DV	03/23/05	Receiving Water	88.9%	103.8%	15.5%
CA0081400	SIERRA PACIFIC, SHASTA LAKE DV	12/30/04	Receiving Water	110.6%	94.1%	16.1%
CA0084140	SWA AT MOUNTAIN GATE	10/19/04	Receiving Water	116.9%	115.6%	1.1%
CA0079154	TRACY WWTP	04/11/05	Receiving Water	104.20%	100.70%	3.4%
CA0079154	TRACY WWTP	08/25/05	Receiving Water	97.10%	93.50%	3.8%
CA0078948	TURLOCK WWTP	08/23/04	Receiving Water	13.3%	12.3%	7.8%
CA0078948	TURLOCK WWTP	08/23/04	Receiving Water	103.0%	83.5%	20.9%
CA0084182	UC DAVIS HYDRAULICS LABORATORY	09/22/04	Receiving Water	116.5%	127.4%	8.9%
CA0083348	UCDAVIS AQUATIC CENTER/ANIMAL SCIENCE	09/22/04	Receiving Water	116.5%	127.4%	8.9%
CA0077933	WILLIAMS WWTP	08/25/04	Receiving Water	90.5%	86.5%	4.5%
CA0077950	WOODLAND WWTP	11/09/04	Receiving Water	93.3%	93.6%	0.3%
CA0079260	YUBA CITY WWTP	10/12/04	Receiving Water	86%	99.40%	14.5%

[a] Effluent and influent data for municipal WWTPs is annotated with "(Mun-WW)".
[b] The Manteca Aggregate Sand Plant is now known as Oakwood Lake Subdivision Mining Reclamation.

APPENDIX D
COMMENTS AND RESPONSES SUBMITTED DURING THE ADMINISTRATIVE DRAFT REVIEW AND PUBLIC DRAFT REVIEW

Following are comments submitted during the Administrative Draft Report and Public Draft Report reviews and staff responses. Comments are in **bold** and staff responses are in plain text.

1. Mike Paulucci (Laboratory Manager), City of Yuba City Utilities Department, Yuba City WWTP (CA0079260) – E-mail dated December 15, 2008

2. William T. Aravanis PE REA (Senior Engineer) and Paul C. Deutsch (Principal Scientist), General Electric Company, Former Kendall Site, Merced, California (CA0081833) – Letter dated December 22, 2008

3. Art O' Brien PE (Wastewater Utility Manager), City of Roseville, Roseville Pleasant Grove and Dry Creek WWTPs (CA0084573 and CA0079502) – Letter dated January 14, 2009

4. Linda Dorn (Business Citizen's Assistant), Sacramento Regional County Sanitation District, Sacramento River and Walnut Grove WWTPs (CA0077682 and CA0078794) – Letter dated January 15, 2009

5. Lysa Voight PE (Senior Civil Engineer), Sacramento Regional County Sanitation District, Sacramento River and Walnut Grove WWTPs (CA0077682 and CA0078794) – Letter dated March 18, 2009

6. Airy Krich-Brinton, Larry Walker Associates – Email dated June 11, 2009

7. Lysa Voight PE (Senior Civil Engineer), Sacramento Regional County Sanitation District, Sacramento River and Walnut Grove WWTPs (CA0077682 and CA0078794) – Letter dated 15 June 2009

1. Mike Paulucci (Laboratory Manager), City of Yuba City Utilities Department, Yuba City WWTP (CA0079260) – Letter dated December 15, 2008

Table 11 on page 52 is missing the Field Duplicate data from our August 2004 sample event. I have attached a copy of the laboratory report. The table should include for the City's August 24, 2004 sample event a duplicate 1 value of 0.036 ng/L and duplicate 2 value of 0.038 ng/L (RPD 5.4%). Yuba City did not conduct field duplicates for September 2004 as properly noted in Table 11.

Table 11 on page 52 also lists both values for the July 5, 2005 sample event as 0.025 ng/L; however, the values should indicate that both sample were not detected at a reporting limit (RL) of 0.025 ng/L or"<0.025 ng/L".

Table 15 on page 62 lists Yuba City's discharge flow as 5.50 MGD. The flow for the sample dates is 5.22 MGD.

Table 19 on page 70 lists Yuba City's discharge flow as 5.50 MGD. The flow for the sample dates is 5.22 MGD.

Table C.1 on page 183 indicates Yuba City collected an influent sample on July 5, 2005. The City did not collect any influent methylmercury samples for this study as influent samples were voluntary as listed in the 13267 Order. The data listed in Table C.1 is from a sample location not related to the methylmercury study and should be removed.

R-1: Staff incorporated all of the corrections into the report.

2. William T. Aravanis PE REA (Senior Engineer) and Paul C. Deutsch (Principal Scientist), General Electric Company, Former Kendall Site, Merced, California (CA0081833) – Letter dated December 22, 2008

Table A.1 includes data for the National Pollutant Discharge Elimination System (NPDES) number CA0083739. That NPDES number was discontinued when NPDES number CA0081833 was issued in July 2004 with provisions to include discharges originally permitted under NPDES number CA0083739. The first round of methylmercury samples were collected in October 2004. Consequently, samples included in the December 2008 letter were not collected subject to NPDES number CA0083739 and reference to this NPDES number should be removed from Table A.1.

R-2: Staff removed the record of the NPDES # CA0083739 from Table A.1, since at the time the 13267 letter was sent, discharges originally covered under permit CA0083739 were included under the permit CA0081833.

Tables B.1 through B.4 contain footnotes (footnotes m, f, g, and c of tables B.1, B.2, B.3, and B.4, respectively)describing reasons that results of samples collected from the site on October 8, 2004, were not included in the tables. These footnotes indicate the samples were contaminated at the laboratory and that hold times were exceeded. However, the footnotes do not clearly indicate that the location where the hold time was exceeded was at the laboratory. For example, footnote m of table B.1 says "However, results for samples collected on 8 October 2004 were not incorporated in the calculations due to sample contamination with mercury in the laboratory and preservation hold times exceeding EPA recommendations." GE requests that the RWQCB revise

the footnote to read "However, results for samples collected on 8 October 2004 were not incorporated in the calculations due to sample contamination with mercury in the laboratory and preservation hold times at the laboratory exceeding EPA recommendations for reanalyzing the samples." This change in wording would remove any ambiguity concerning where the samples were located when hold times were exceeded.

R-3: After looking at the Semiannual Monitoring Report sent on 21 February 2005, it does not appear that Brooks Rand was able to reanalyze the contaminated samples after the GE request because the remaining sample was contaminated as well. Therefore, staff revised the footnotes in Tables B.1 through B.4 to state: "However, results for samples collected on 8 October 2004 were not incorporated in the calculations due to sample contamination with mercury in the laboratory and preservation hold times at the laboratory exceeding EPA recommendations."

3. Art O' Brien PE (Wastewater Utility Manager), City of Roseville, Roseville Pleasant Grove and Dry Creek WWTPs (CA0084573 and CA0079502) – Letter dated January 14, 2009

Thank you for the opportunity to comment on the subject report. The comments are outlined below:

1. Page 26, 2nd full paragraph: "The denitrification process involves anaerobic bacteria converting nitrate to nitrogen gas with the help of methanol (Metcalf and Eddy, Inc., 1972)." This is likely an incorrect reference quote. First, at our WWTPs, the anoxic bacteria convert the nitrate to nitrogen gas. Second, not all WWTPs use methanol as the carbon source for the denitrification process. We do not add methanol as a carbon source. Third, a carbon source is only needed when the denitrification process follows the nitrification process. This sentence should be changed to: "The denitrification process involves anoxic bacteria converting nitrate to nitrogen gas with the help of a carbon source such as methanol (Metcalf and Eddy, Inc., 1972)."

R-4: Staff agrees with the suggested sentence change and modified the sentence in the report accordingly.

2. Table 19 (page 69): PGWWTP should have box 15 and 19 marked off
DCWWTP should have box 15 marked off

R-5: Staff made the suggested changes in Table 19. The Roseville Pleasant Grove WWTP was already placed in the "N/D + Filtration + Chlor./ Dechlor." treatment category, so the effluent methylmercury analysis for the various categories did not need to be redone.

3. Some of the data and statistical analyses do not support the conclusions:

- **Section 4.2.5, pg 30, 2nd full paragraph: the authors conclude there is a "significant positive relationship (R^2=0.1347, Figure 28a and R^2=0.0715, Figure 28b)" between influent methylmercury and effluent methylmercury. The authors go on to state: "These significant relationships indicate that reductions in methylmercury in the effluent were in part due to lower influent concentrations." This conclusion is not supported by the statistical analysis. The extremely low R^2 value would draw the exact opposite conclusion. R^2 is the square of the correlation coefficient or coefficient of determination. This statistical method is a good way of evaluating the strength of the relationship**

between 2 variables and is measure between 0 and 1. When R^2=1, there is a very strong relationship, conversely when R^2=0, a weak relationship exists. Therefore, it appears that these data demonstrates a very weak relationship at best.

R-6: Staff agrees that there is a weak relationship between influent methylmercury and effluent methylmercury indicated by the low R^2 values (square of the correlation coefficient). R^2 is the proportion of the variance of "variable y" that can be explained by the "variable x". Staff discussed this in the last sentence of the 2nd full paragraph on page 30: "…7-13% of the variability in effluent methylmercury concentrations was explained by influent concentrations, indicating that effluent concentrations were affected by other factors as well." Even though both of the relationships shown in Figures 28a and 28b have low R^2 values, they are statistically significant with p-values (two-sided levels of significance) less than 0.0001 using the one-sample t-test for the correlation coefficient (R). Typically, p-values less than 0.05 are considered statistically significant. The reason that the relationships have low R^2 values and are still significant is in part due to the large number of paired data points in each relationship. Figure 28a, which is the scatter plot of all paired data from all WWTPs excluding SRCSD Sacramento River WWTP, has 131 paired data points. Figure 28b, which includes the SRCSD Sacramento River WWTP paired data, has 238.

- **Section 4.2.6, pages 31 and 32: the authors draw the same "significant positive relationship" conclusion as was done in section 4.2.5. These data, again, resulted in extremely low R^2 values indicating that there is very low correlation between effluent methylmercury and effluent total mercury.**

R-7: Staff agrees that the relationships referred to in this comment are weakly correlated. However, all of these relationships have p-values less than 0.01 using the one-sample t-test for the correlation coefficient (R), which indicates statistical significance. See comment R-6 for further explanation.

- **Section 4.2.7, 3rd paragraph, page 32 and Section 4.2.8, 3rd paragraph, page 33: the authors conclude that there is no relationship between effluent methylmercury and influent total mercury. However, no statistical analysis (i.e. R^2 values) is presented that support these conclusions.**

R-8: Staff added the R^2 values and p-values to the text in the report referring to these relationships. All of the effluent methylmercury vs. influent inorganic Mercury and effluent vs. influent inorganic Mercury relationships had p-values greater than 0.05, indicating no statistical significance.

4. General observations:

- **The authors appear to work very hard at trying to draw statistically "significant" conclusions from this data using statistical modeling. This leaves the impression they are trying to make the data support a preconceived conclusion. Based on the data and the statistical analysis performed, the only conclusions that can be drawn are:**

    1. **Low levels of methylmercury exist in some WWTP's influent and effluent; however, a relationship can not be drawn.**

    2. **Low levels of total methylmercury exist in some WWTP's influent and effluent. Removal efficiencies can be determined.**

3. **The type of WWTP treatment process may influence the removal efficiency.**

4. **Seasonality may or may not play a role in methylmercury concentrations.**

R-9: One of the questions the Central Valley Water Board (Board) staff posed and analyzed in this report was: "Does a relationship exist between WWTP treatment processes and effluent methylmercury concentrations? Do WWTPs with a particular treatment process have higher effluent concentrations than WWTPs with other treatment processes?" In order to answer these questions, staff developed 10 mutually exclusive treatment categories based on secondary, tertiary and disinfectant treatment types. Pond and nitrification/denitrification treatments were considered separately from other types of secondary treatment types because they are significantly different from other treatments and could have an effect on effluent methylmercury concentrations. The categories were internally reviewed and verified by multiple Board engineers in the NPDES permitting unit who are very knowledgeable about WWTP treatment processes. Each WWTP that submitted effluent methylmercury data was assigned to one of these 10 categories and the data for all of the WWTPs in each category were grouped together for the analysis. Differences between the treatment categories were analyzed using a nonparametric multiple comparison procedure and the results were presented in the report. Staff allowed for the robust statistical test used to conclude the differences between the treatment categories and did not bias the test and results in any way. A similar procedure was used to compare effluent:influent methylmercury ratios, effluent inorganic Mercury:methylmercury ratios and the 3 secondary subcategories within the "Secondary + C/D" and "Filtration + C/D" categories.

- **The last paragraph of the report is of great concern (pg 38, 39): "additional monitoring studies and pilot projects". To require municipalities, under the auspices of AB13267, to provide personnel and funding to support this massive data acquisition could be problematic. Due to the limited resources and reduced budgets we are operating under, it would present real challenges to support this project both financially and from a personnel standpoint. Sampling for these constituents and performing the associated analyses is very expensive.**

R-10: The full paragraph (pg 38, 39) is: "Several Central Valley WWTP staff and consultants have noted that it would be very helpful to establish a working group that coordinates efforts between CVCWA, San Francisco Bay area facilities, and other regional efforts to develop more detailed analyses of the existing information, further evaluate treatment processes, and design additional monitoring studies and pilot projects. Board staff is supportive of this concept and will work with dischargers and working groups to design and review studies." Board staff appreciates the financial and personnel challenges of conducting additional studies and pilot projects. It is possible that this report's results may be used to support additional studies during the implementation phase of the Delta mercury control program and other upstream mercury control programs. As noted in the February 2008 draft Basin Plan amendment staff report[1] and in later responses to public comments,[2] Board staff recommends that, during the implementation phase of the Delta mercury control program, entities responsible for point and nonpoint sources conduct collaborative and coordinated control studies. During the time of this report, Board staff has been working with stakeholders to develop an efficient and cost effective mercury control program.

[1] Available at: http://www.waterboards.ca.gov/centralvalley/water_issues/tmdl/central_valley_projects/delta_hg/staff_report_feb08/index.shtml

[2] Available at: http://www.waterboards.ca.gov/centralvalley/water_issues/tmdl/central_valley_projects/delta_hg/stakeholder_meetings/25nov08_hearing_rtc.pdf

- **Our overarching concern is that further study and/or further regulation of WWTPs regarding methylmercury will not reduce the concentrations of mercury in fish tissue. It is important to provide a clear conclusion on this point in this report. As research has shown, and the authors actually cite in the second sentence of the Executive Summary, methylmercury only accounts for 1% of all mercury discharged to the Delta. Therefore removing 100% of the 1% isn't even statistically significant and wouldn't begin to address the problem. Also it should be noted, that all the WWTPs that discharge to the Delta account for less than 2% of the total mercury in the Delta. Again if 100% of the 2% were removed, no significant impact in reducing the mercury in the Delta would be realized.**

R-11: Of the approximately 400 kg inorganic Mercury that enters the Delta each year, about 2.2 kg is methylmercury. Although methylmercury is less than 1% of all mercury discharged to the Delta, methylmercury is the form that accumulates in the food web. If there were no methylmercury in Delta waters (i.e., if the 1% of all mercury discharged to the Delta that is in the form of methylmercury were demethylated), there would be no fish impairment.

The best available science indicates that reducing methylmercury in ambient water is the most direct way to reduce methylmercury in biota. Methylmercury is produced by many modern-day activities that humans may be able to modify so that less methylmercury is discharged. The Delta control program could focus on reducing methylmercury sources by reducing the inorganic mercury that supplies the methylation sites (i.e., reduce the inorganic mercury levels in Delta sediments by reducing discharges from mine sites and other legacy and modern sources) and by managing the methylation sources themselves to reduce methylmercury discharges. As part of their recommendations for a Delta mercury control program, Board staff recommended that WWTPs, MS4s, wetlands, irrigated agriculture, and new water management activities evaluate and develop management practices to reduce their methylmercury loads, such that each takes responsibility for its contribution to the impairment. As noted earlier, staff does not recommend that every individual NPDES, MS4, and agricultural and wetland landowner individually conduct a study, but instead recommends coordinated studies.

The stakeholder process for the Delta mercury control program will be developing an adaptive management approach to address the methylmercury impairment. Without the completion of point and nonpoint methylmercury control studies, it is not yet possible to define which sources are "important" or "insignificant" or which are feasible or make sense to control. When discussing the importance of different sources, many stakeholders have focused on the amount of loading by source category and by individual discharge. However, there are additional factors that should be considered. Given the number of individual discharges there are in each source category in the Delta, almost all of the individual discharges are small. Although the tributary inputs are substantial, available information indicates that they also contain a similar distribution of individual discharges. As determined as early as 1997 in the Sacramento River Mercury Control Planning Project report prepared for SRCSD by Larry Walker Associates, "… mercury sources in the study area appear to be diffusely distributed without any significant "hotspots" …" (LWA, 1997, page 31). Examples of small discharges include most wastewater treatment plants (which comprise about 4% of methylmercury inputs to the Delta), individual farm fields, and wetlands where water flow is managed in discrete units. It is the sum of all of the individual discharges (point and non-point) in the Delta and its tributary watersheds that impairs the Delta. The "importance" or "insignificance" of different methylmercury and inorganic Mercury sources could be defined by: (a) their load, (b) their distance from an impaired area, (c) how big of a reduction is needed to achieve safe fish mercury levels in a given impaired area, (d) whether they can be controlled, (e) whether they can be controlled without impacting habitat or operational function, (f) the cost to control them, and (g) the resources available to the

responsible parties to implement controls. It is conceivable that the control program for the Delta will need to focus on just a few large projects in some watersheds, but many small projects in other watersheds, to reduce methylmercury levels throughout the Delta.

Please refer to the February 2008 draft Basin Plan amendment and Delta TMDL staff reports[3] and the follow-up document, "Staff's Initial Responses to Board and Stakeholder Questions and Comments at the April 2008 Hearing"[4], for additional discussion on this topic.

4. Linda Dorn (Business Citizen's Assistant), Sacramento Regional County Sanitation District, Sacramento River and Walnut Grove WWTPs (CA0077682 and CA0078794) – Letter dated January 15, 2009

SRCSD submitted two letters (attached), which included three lab reports, to the RWQCB within the required monitoring period. The three sampling dates are: 12/29/2004, 1/20/2005, and 4/6/2005. The data presented in the report only includes two sampling results rather than the three submitted. The sample result for 12/29/04 is missing. Including this result will decrease the average effluent methylmercury concentration from 2.16 ng/L to 1.69 ng/L. The average methylmercury concentration in discharge is presented in Tables 18 and 19 of the administrative draft of the staff report.

R-12: The sample collected on 29 December 2004 was excluded from calculations made in the report because the hold time between collection and preservation exceeded 60 hours. This is consistent with all other samples that exceeded 60 hours hold times. The effluent sample collected on 29 December 2004 arrived at Frontier Geosciences on 3 January 2005 and was preserved with acid upon receipt. This is approximately 120 hours between collection and preservation. USEPA Method 1630 (methylmercury analysis in water) requires samples to be preserved with acid within 48 hours to a pH of less than two. Acid preservation stops the bacterial activity in the water that produces methylmercury from inorganic mercury. Samples without preservation may not be representative of the conditions at the time of sampling if bacterial activity continues after sampling. Therefore, staff excluded data for all samples whose hold times exceeded 60 hours.

5. Lysa Voight PE (Senior Civil Engineer), Sacramento Regional County Sanitation District, Sacramento River and Walnut Grove WWTPs (CA0077682 and CA0078794) - Letter dated March 18, 2009

Page 116, Figure 25 and Page 122 Figure 29B: SRCSD requests that a note be added to the figures indicating that three points of data were provided, but only two were used in this report for the SRCSD Walnut Grove WWTP. This might also be explained in section 3.6 anomalous values. A suggested wording for the footnote is: "Three data points were provided, but only two data points were used. The third data point was not considered in this report due to receipt of the

[3] Available at: http://www.waterboards.ca.gov/centralvalley/water_issues/tmdl/central_valley_projects/delta_hg/staff_report_feb08/index.shtml

[4] Available at: http://www.waterboards.ca.gov/centralvalley/water_issues/tmdl/central_valley_projects/delta_hg/stakeholder_meetings/25nov08_hearing_rtc.pdf

sample beyond the 48 hour holding period at an elevated temperature as noted on the lab's transmittal memo."

R-13: Staff added a new table (Table 11) to the report to provide the methylmercury data that were excluded from the report's calculations due to quality control concerns (e.g., hold time exceedances greater than 60 hours and laboratory contamination). This table includes the effluent sample collected at SRCSD Walnut Grove WWTP on 29 December 2004. Section 3.2 (page 13) in the revised report refers to Table 11. Samples that do not meet quality control requirements may not be representative of the conditions at the time of sampling. Therefore, including excluded data in calculations could be misleading.

P.22: The statement "Municipal WWTPs may contribute significant methylmercury loads to receiving water" perpetuates the misperception that WWTPs are major sources of the total methylmercury to the river. This report and its analysis are focused on NPDES permit holders which are a small portion of the total and methylmercury loading. All loads to receiving water are not compared in this report so care should be used when referencing whether or not WWTP loading is significant. A more appropriate statement that SRCSD suggests is: "Municipal WWTPs appear to contribute a greater methylmercury load to receiving water when compared to the other permitted sources investigated in this report but are a small fraction of the total and methylmercury load in the Sacramento River and the Delta."

R-14: Staff edited the beginning of Section 4.2.

P.29-30: The paired influent-effluent samples should be qualified more by mention of the following note that SRCSD recommends adding to the second paragraph of page 30: "The paired samples do not necessarily represent the same parcels of water due to in-plant residence time."

R-15: Staff added the suggested text to the report.

P.38: An additional question that might be addressed by future analysis is suggested as follows: "Do other factors impact reported concentrations, such as sampling protocols including location, time of day, holding time, composite vs. grab samples?"

R-16: Staff added the suggested text to the report.

Executive Summary: SRCSD suggests that the following comment be added to the executive summary so that readers understand the relationship between discharge and receiving waters: "The concentration of mercury and methylmercury in waters is dynamic. Mercury methylates and demethylates as a function of several factors including the characteristics of the effluent stream and the characteristics of the receiving waters. The mercury/methylmercury inter-relationships are currently being studied by various stakeholders but are not fully understood at the time of the completion of this report."

R-17: Staff edited the Executive Summary.

6. Airy Krich-Brinton, Larry Walker Associates – Email dated June 11, 2009 sent to Michelle Wood (Environmental Scientist, Central Valley Water Board)

I have been using the data file you sent and checking the statistical calculations shown in the methyl mercury report, and I have a question. In Table 24 (and similar tables), the title indicates that a Kruskal-Wallis Multiple Comparison was performed on median values. However, that test only produces a single p-value, and the table is populated with multiple p-values, one for each

treatment category pair. Can you explain further how those p-values were calculated? The footnote states that they are two-sided significance levels multiplied by 36, but it does not tell how the significance levels are determined (what test was used). Can you help me find out which test was used to calculate the p-values in tables like Table 24?

R-18: Table 24 and similar tables report the p-values for the Kruskal-Wallis Multiple Comparison test run in the Statistica software. Basically, you run a Kruskal Wallis test and if you find that there are significant differences between medians then you have to run a multiple comparison test to identify which medians are responsible for the statistical difference. The documentation from Statistica (see attached) is the best way to determine the type of multiple comparison test used. Most likely it is a Dunn's comparison procedure. With Statistica you can set the test for a default p value. We used a traditional value of $p < 0.05$ as the cut off. However, the program will give you actual p-values, which is what we reported. Also, Table 24 and similar tables report two p-values for each pair comparison, which are actually identical when looking closely. We set the table up this way to make it easier to identify the p-values for a particular pair of treatment categories. [Response provided in a 12 June 2009 email.]

7. Lysa Voight PE (Senior Civil Engineer), Sacramento Regional County Sanitation District, Sacramento River and Walnut Grove WWTPs (CA0077682 and CA0078794) – Letter dated June 15, 2009

Thank you for the opportunity to review the final version of the subject document and for taking into account our comments from the previous draft version of the document. The following comments are being provided by SRCSD to help put the report's findings in a context that is useful for policy and regulatory efforts such as the Delta Mercury TMDL.

In the Executive Summary and in the Introduction, the low aggregate contribution of methylmercury to the Delta by NPDES permitted facilities should be clearly stated. The report refers to the relative contributions from different NPDES permitted sources, but does not provide important information regarding the numerical or quantitative significance of the sum of the point sources in the Delta relative to the entire methylmercury impairment.

R-19: The Administrative and Public Review drafts of this report focused on a review of effluent methylmercury concentrations and did not attempt to calculate effluent methylmercury loads for the more than 100 facilities in the Central Valley. However, staff agrees that having load estimates will be useful for the Delta and upstream TMDL development efforts. To address SRCSD's comment, staff added a new chapter to the report (Chapter 5) that includes a method for calculating methylmercury loads discharged by NPDES facilities within the Delta and its upstream watersheds, and compares the sum of those loads to overall methylmercury loading to the Delta by watershed.

Page 22, Section 4.2: The report cites older data for the SRWTP and states that methylmercury loads as a percentage of receiving water loads "was as high as 30 to 43% during the warm seasons of 2001 and 2002". Page 91 of the report shows a graphical representation of the percentage of methylmercury in SRWTP discharge compared to the Sacramento River. The two points selected for discussion are not typical values for the stated time period. Many of the points reported for years 2000-2006 indicate the SRWTP contribution to methylmercury is under 10%.

R-20: The entire sentence in the report is, "For example, a six-year comparison of the SRCSD Sacramento River WWTP effluent methylmercury loads as a percentage of its receiving

water loads was as high as 30 to 43% during the warm seasons of 2001 and 2002 and less than 1% during the wet seasons of 2005 and 2006 (Figure 4; Bosworth, 2008), ranging from 4.2% to 17% on an annual basis." The purpose of the text is to highlight the range of conditions as well as typical conditions. Also, although the three high points mentioned in the text (30%, 31%, and 43%) are not typical values, they are not anomalously high, given that there were 14 other points that fell between 20% and 30%. No changes were made to the text.

In the absence of an actual conclusive analysis, a general statement regarding the ability to reduce methylmercury levels in water through point source controls is questionable.

R-21: Staff assumes that SRCSD is referring to the sentence that follows the above mentioned percent range, at the end of the last paragraph on Page 22 of the draft report: "For some receiving waters, reducing municipal WWTP methylmercury discharges, along with other point and nonpoint sources, may be an important component in reducing methylmercury levels in water." Staff was careful to include both point and nonpoint sources in this general sentence. Until the proposed Phase 1 control studies are conducted, we cannot know for certain which point and nonpoint sources can be feasibly and reasonably reduced. However, it seems reasonable to note that reducing municipal WWTP methylmercury discharges may be an important component, especially for individual water bodies that are dominated by effluent from municipal WWTPs or for which municipal WWTP discharges comprise a substantial source. For example, the Sacramento River is the largest river in California and drains a 27,000 square-mile area – almost one fifth of the State of California and about one half of the Central Valley – that contains numerous reservoirs and a myriad of point and nonpoint sources downstream of the reservoirs. As noted as early as 1997 in the Sacramento River Mercury Control Planning Project report prepared for SRCSD by Larry Walker Associates, "… mercury sources in the study area appear to be diffusely distributed without any significant "hotspots" …" (LWA, 1997, page 31). As a result, any individual discharge from a point or nonpoint source that provides a notable percentage (e.g., more than 1%) of methylmercury loading to the Sacramento River warrants evaluation.

It should be noted in the report that methylmercury is not strictly bioavailable mercury nor is it conservative.

R-22: Staff edited the Introduction to reflect that methylmercury is the most bioaccumulated form of mercury, rather than most bioavailable. In addition, staff added text to further describe degradation processes, as well as how in some waterways processes of methylmercury production and transport downstream in the water column are dominant and in others, processes that remove methylmercury from the water column such as photodegradation and sedimentation are dominant, and included the results of SRCSD's 2008 Localized Mercury Bioaccumulation Study.

The Water Environment Research Foundation (WERF) recently completed a study of mercury bioavailability discharged from conventional municipal wastewater treatment plants. The WERF research is part of the difficult process of understanding the relationship between total mercury methylmercury and bioavailable mercury, all of which should be considered when evaluating the TMDL.

R-23: Staff agrees and, in response to this comment, staff added the following text to Chapter 6: "… at the time this report was receiving final review, reports for Phases 1 and 2 of the WERF-funded project, "Estimation of Mercury Bioaccumulation Potential from Wastewater

Treatment Plants in Receiving Waters", were released (Dean and Mason, 2009a and 2009b). This project assessed changes in mercury bioavailability in wastewater effluents and receiving waters and developed a guidance document for wastewater treatment professionals who want to assess the bioavailability of mercury in their wastewater, compare it to other point and nonpoint sources, and assess changes in bioavailability in their effluent when it is mixed in a receiving water body. The Phase 1 and 2 reports should be considered by future wastewater analyses and control studies, as well as when the Delta mercury TMDL control program goes through future reviews."

SRCSD previously commented with an objection to the use of the term "significant positive relationship" between paired influent and effluent data with low R^2 values (low model reliability). The Regional Board responded by stating that the low p-values associated with the results allow this term. While it is correct to say that a low p-value indicates statistical significance, the low R-values indicate that the fit of the model cannot be trusted more than "R-value" percent of the time. Thus, the model is not a good predictor on an individual basis.

R-24: Staff assumes that SRCSD is referring to the comment made by Art O' Brien (Wastewater Utility Manager, City of Roseville), and staff's response regarding how paired influent/effluent data with low R^2 values can have low p-values, indicating statistical significance (staff response R-6, page 192 in this appendix). As noted in staff's response, staff agrees that there is a weak relationship between influent methylmercury and effluent methylmercury indicated by the low R^2 values, and further that influent methylmercury concentration alone is not a good predictor of effluent methylmercury on an individual basis. This is why staff had included the following text in earlier drafts, "…7-13% of the variability in effluent methylmercury concentrations was explained by influent concentrations, indicating that effluent concentrations were affected by other factors as well." Staff added the word "substantially" ("were substantially affected") in attempt to more clearly indicate that staff is not stating that influent methylmercury alone is a good predictor, and carefully included similar text wherever low R^2 values were associated with paired data that also had low p values.

United States
Environmental Protection
Agency

Office of Water
Office of Science and Technology
4304

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Methodology for Deriving Ambient Water Quality Criteria for the Protection of Human Health (2000)

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Methodology for Deriving Ambient Water Quality Criteria for the Protection of Human Health (2000)

Final

Office of Science and Technology
Office of Water
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Washington, DC 20460

NOTICE

The policies and procedures set forth in this document are intended solely to describe EPA methods for developing or revising ambient water quality criteria to protect human health, pursuant to Section 304(a) of the Clean Water Act, and to serve as guidance to States and authorized Tribes for developing their own water quality criteria. This guidance does not substitute for the Clean Water Act or EPA's regulations; nor is it a regulation itself. Thus, it does not impose legally-binding requirements on EPA, States, Tribes or the regulated community, and may not apply to a particular situation based upon the circumstances.

This document has been reviewed in accordance with U.S. Environmental Protection Agency policy and approved for publication. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

FOREWORD

This document presents EPA's recommended Methodology for developing ambient water quality criteria as required under Section 304(a) of the Clean Water Act (CWA). The Methodology is guidance for scientific human health assessments used by EPA to develop, publish, and from time to time revise, recommended criteria for water quality accurately reflecting the latest scientific knowledge. The recommended criteria serve States and Tribes' needs in their development of water quality standards under Section 303(c) of the CWA.

The term "water quality criteria" is used in two sections of the Clean Water Act, Section 304(a)(1) and Section 303(c)(2). The term has a different program impact in each section. In Section 304, the term represents a scientific assessment of ecological and human health effects that EPA recommends to States and authorized Tribes for establishing water quality standards that ultimately provide a basis for controlling discharges or releases of pollutants. Ambient water quality criteria associated with specific stream uses when adopted as State or Tribal water quality standards under Section 303 define the maximum levels of a pollutant necessary to protect designated uses in ambient waters. The water quality criteria adopted in the State or Tribal water quality standards could have the same numerical limits as the criteria developed under Section 304. However, in many situations States and authorized Tribes may want to adjust water quality criteria developed under Section 304 to reflect local environmental conditions and human exposure patterns before incorporation into water quality standards. When adopting their water quality criteria, States and authorized Tribes have four options: (1) adopt EPA's 304(a) recommendations; (2) adopt 304(a) criteria modified to reflect site-specific conditions; (3) develop criteria based on other scientifically defensible methods; or (4) establish narrative criteria where numeric criteria cannot be determined.

EPA will use this Methodology to develop new ambient water quality criteria and to revise existing recommended water quality criteria. It also provides States and authorized Tribes the necessary guidance to adjust water quality criteria developed under Section 304 to reflect local conditions or to develop their own water quality criteria using scientifically defensible methods consistent with this Methodology. EPA encourages States and authorized Tribes to use this Methodology to develop or revise water quality criteria to appropriately reflect local conditions. EPA believes that ambient water quality criteria inherently require several risk management decisions that are, in many cases, better made at the State, Tribal, or regional level. Additional guidance to assist States and authorized Tribes in the modification of criteria based on the Methodology will accompany this document in the form of three companion Technical Support Documents on Risk Assessment, Exposure Assessment, and Bioaccumulation Assessment.

_____

Geoffrey H. Grubbs
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Potential areas for conflict of interest were investigated via direct inquiry with the peer reviews and review of their current affiliations. No conflicts of interest were identified.

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LIST OF ACRONYMS

ADI	Acceptable Daily Intake
ARAR	Applicable or Relevant and Appropriate Requirements
ASTM	American Society of Testing and Materials
AWQC	Ambient Water Quality Criteria
BAF	Bioaccumulation Factor
BAF_{ℓ}^{fd}	Baseline Bioaccumulation Factor
BCF	Bioconcentration Factor
BCF_{ℓ}^{fd}	Baseline Bioconcentration Factor
$BCF_{\mathbf{T}}^{\mathbf{t}}$	Bioconcentration Factor Based on Total Concentrations in Tissue and Water
BMD	Benchmark Dose
BMDL	Lower-Bound Confidence Limit on the BMD
BMF	Biomagnification Factor
BMR	Benchmark Response
BSAF	Biota-Sediment Accumulation Factors
BW	Body Weight
C_{ℓ}	Lipid-normalized Concentration
C_{soc}	Organic Carbon-normalized Concentration
C_t	Concentration of the Chemical in the Specified Wet Tissue
C_w	Concentration of the Chemical in Water
CDC	U.S. Centers for Disease Control and Prevention
CSFII	Continuing Survey of Food Intake by Individuals
CWA	Clean Water Act
DDT	1,1,1-trichloro-2,2-bis(p-chlorophenyl)ethane
DDE	1,1-dichloro-2,2-bis(p-chlorophenyl)ethylene
DDD	1,1-dichloro-2,2-bis(p-chlorophenyl)ethane
DI	Drinking Water Intake
DNA	Deoxyribonucleic Acid
DNOC	2,4-dinitro-o-cresol
DOC	Dissolved Organic Carbon
ED_{10}	Dose Associated with a 10 Percent Extra Risk
EPA	Environmental Protection Agency
f_{fd}	Fraction Freely Dissolved
f_{ℓ}	Fraction Lipid
FCM	Food Chain Multiplier
FEL	Frank Effect Level
FI	Fish Intake
FIFRA	Federal Insecticide, Fungicide, and Rodenticide Act
GLI	Great Lakes Water Quality Initiative
HCBD	Hexachlorobutadiene
IARC	International Agency for Research on Cancer
II	Incidental Ingestion
ILSI	International Life Sciences Institute

IRIS	Integration Risk Information System
kg	kilogram
K_{ow}	Octanol-Water Partition Coefficient
L	Liter
LAS	Linear Alkylbenzesulfonate
LED_{10}	The Lower 95 Percent Confidence Limit on a Dose Associated with a 10 Percent Extra Risk
LMS	Linear Multistage Model
LOAEL	Lowest Observed Adverse Effect Level
M_ℓ	Mass of Lipid in Specified Tissue
M_t	Mass of Specified Tissue (Wet Weight)
MCL	Maximum Contaminant Level
MCLG	Maximum Contaminant Level Goal
MF	Modifying Factor
mg	Milligrams
ml	Milliliters
MOA	Mode of Action
MOE	Margin of Exposure
NCHS	National Center for Health Statistics
NCI	National Cancer Institute
NFCS	Nationwide Food Consumption Survey
NHANES	National Health and Nutrition Examination Survey
NOAEL	No Observed Adverse Effect Level
NOEL	No Observed Effect Level
NPDES	National Pollutant Discharge Elimination System
PAH	Polycyclic Aromatic Hydrocarbon
PCB	Polychlorinated Biphenyls
POD	Point of Departure
POC	Particulate Organic Carbon
RDA	Recommended Daily Allowance
RfC	Reference Concentration
RfD	Reference Dose
RfD_{DT}	Reference Dose for Developmental Effects
RPF	Relative Potency Factor
RSC	Relative Source Contribution
RSD	Risk-Specific Dose
SAB	Science Advisory Board
SDWA	Safe Drinking Water Act
SF	Safety Factor
STORET	Storage Retrieval
TEAM	Total Exposure Assessment Methodology
TEF	Toxicity Equivalency Factor
TMDL	Total Maximum Daily Load
TSD	Technical Support Document
USDA	United States Department of Agriculture
USEPA	United States Environmental Protection Agency

UF	Uncertainty Factor
WQBEL	Water Quality-Based Effluent Limits

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1. INTRODUCTION

1.1 WATER QUALITY CRITERIA AND STANDARDS

Pursuant to Section 304(a)(1) of the Clean Water Act (CWA), the U.S. Environmental Protection Agency (EPA) is required to publish, and from time to time thereafter revise, criteria for water quality accurately reflecting the latest scientific knowledge on the kind and extent of all identifiable effects on human health which may be expected from the presence of pollutants in any body of water.

Historically, the ambient water quality criteria (AWQC or 304(a) criteria) provided two essential types of information: (1) discussions of available scientific data on the effects of the pollutants on public health and welfare, aquatic life, and recreation; and (2) quantitative concentrations or qualitative assessments of the levels of pollutants in water which, if not exceeded, will generally ensure adequate water quality for a specified water use. Water quality criteria developed under Section 304(a) are based solely on data and scientific judgments on the relationship between pollutant concentrations and environmental and human health effects. The 304(a) criteria do not reflect consideration of economic impacts or the technological feasibility of meeting the criteria in ambient water. These 304(a) criteria may be used as guidance by States and authorized Tribes to establish water quality standards, which ultimately provide a basis for controlling discharges or releases of pollutants into ambient waters.

In 1980, AWQC were derived for 64 pollutants using guidelines developed by the Agency for calculating the impact of waterborne pollutants on aquatic organisms and on human health. Those guidelines consisted of systematic procedures for assessing valid and appropriate data concerning a pollutant's acute and chronic adverse effects on aquatic organisms, nonhuman mammals, and humans.

1.2 PURPOSE OF THIS DOCUMENT

The *Methodology for Deriving Ambient Water Quality Criteria for the Protection of Human Health (2000)* (hereafter the "2000 Human Health Methodology") addresses the development of AWQC to protect human health. The Agency intends to use the 2000 Human Health Methodology both to develop new AWQC for additional pollutants and to revise existing AWQC. Within the next several years, EPA intends to focus on deriving AWQC for chemicals of high priority (including, but not limited to, mercury, arsenic, PCBs, and dioxin). Furthermore, EPA anticipates that 304(a) criteria development in the future will be for bioaccumulative chemicals and pollutants considered highest priority by the Agency. The 2000 Human Health Methodology is also intended to provide States and authorized Tribes flexibility in establishing water quality standards by providing scientifically valid options for developing their own water quality criteria that consider local conditions. States and authorized Tribes are strongly encouraged to use this Methodology to derive their own AWQC. However, the 2000 Human Health Methodology also defines the default factors EPA intends to use in evaluating and determining consistency of State water quality standards with the requirements of the CWA. The Agency intends to use these default factors to calculate national water quality criteria under

Section 304(a) of the Act. EPA will also use this Methodology as guidance when promulgating water quality standards for a State or Tribe under Section 303(c) of the CWA.

This Methodology does not substitute for the CWA or EPA's regulations; nor is it a regulation itself. Thus, the 2000 Human Health Methodology cannot impose legally-binding requirements on EPA, States, Tribes or the regulated community, and may not apply to a particular situation based upon the circumstances. EPA and State/Tribal decision-makers retain the discretion to use different, scientifically defensible, methodologies to develop human health criteria on a case-by-case basis that differ from this Methodology where appropriate. EPA may change the Methodology in the future through intermittent refinements as advances in science or changes in Agency policy occur.

The 2000 Human Health Methodology incorporates scientific advancements made over the past two decades. The use of this Methodology is an important component of the Agency's efforts to improve the quality of the Nation's waters. EPA believes the Methodology will enhance the overall scientific basis of water quality criteria. Further, the Methodology should help States and Tribes address their unique water quality issues and risk management decisions, and afford them greater flexibility in developing their water quality programs.

There are three companion Technical Support Document (TSD) volumes for the 2000 Human Health Methodology: a Risk Assessment TSD; an Exposure Assessment TSD; and a Bioaccumulation TSD. These documents are intended to further support States and Tribes in developing AWQC to reflect local conditions. The Risk Assessment TSD (USEPA, 2000) is being published concurrently with this Methodology. Publication of the Exposure Assessment and Bioaccumulation TSDs are anticipated in 2001.

1.3 HISTORY OF THE AMBIENT WATER QUALITY CRITERIA (AWQC) METHODOLOGY

In 1980, EPA published AWQC for 64 pollutants/pollutant classes identified in Section 307(a) of the CWA and provided a methodology for deriving the criteria (USEPA, 1980). These 1980 AWQC National Guidelines (or the "1980 Methodology") for developing AWQC for the protection of human health addressed three types of endpoints: noncancer, cancer, and organoleptic (taste and odor) effects. Criteria for protection against noncancer and cancer effects were estimated by using risk assessment-based procedures, including extrapolation from animal toxicity or human epidemiological studies. Basic human exposure assumptions were applied to the criterion equation.

The risk assessment-based procedures used to derive the AWQC to protect human health were specific to whether the endpoint was cancer or noncancer. When using cancer as the critical risk assessment endpoint (which had been assumed not to have a threshold), the AWQC were presented as a range of concentrations associated with specified incremental lifetime risk

levels[1]. When using noncancer effects as the critical endpoint, the AWQC reflected an assessment of a "no-effect" level, since noncancer effects were assumed to have a threshold. The key features of each procedure are described briefly in the following paragraphs.

Cancer effects. If human or animal studies on a contaminant indicated that it induced a statistically significant carcinogenic response, the 1980 AWQC National Guidelines treated the contaminant as a carcinogen and derived a low-dose cancer potency factor from available animal data using the linearized multistage model (LMS). The LMS, which uses a linear, nonthreshold assumption for low-dose risk, was used by the Agency as a science policy choice in protecting public health, and represented a plausible upper limit for low-dose risk. The cancer potency factor, which expresses incremental, lifetime risk as a function of the rate of intake of the contaminant, was then combined with exposure assumptions to express that risk in terms of an ambient water concentration. In the 1980 AWQC National Guidelines, the Agency presented a range of contaminant concentrations corresponding to incremental cancer risks of 10^{-7} to 10^{-5} (that is, a risk of one additional case of cancer in a population of ten million to one additional cancer case in a population of one hundred thousand, respectively).

Noncancer effects. If the pollutant was not considered to have the potential for causing cancer in humans (later defined as a known, probable, or possible human carcinogen by the 1986 *Guidelines for Carcinogen Risk Assessment,* USEPA, 1986d), the 1980 AWQC National Guidelines treated the contaminant as a noncarcinogen; a criterion was derived using a threshold concentration for noncancer adverse effects. The criteria derived from noncancer data were based on the Acceptable Daily Intake (ADI) (now termed the reference dose [RfD]). ADI values were generally derived using a no-observed-adverse-effect level (NOAEL) from animal studies, although human data were used whenever available. The ADI was calculated by dividing the NOAEL by an uncertainty factor to account for uncertainties inherent in extrapolating limited toxicological data to humans. In accordance with the National Research Council recommendations of 1977 (NRC, 1977), safety factors (SFs) (later redefined as uncertainty factors) of 10, 100, or 1,000 were used, depending on the quality of the data.

Organoleptic effects. Organoleptic characteristics were also used in developing criteria for some contaminants to control undesirable taste and/or odor imparted by them to ambient water. In some cases, a water quality criterion based on organoleptic effects would be more stringent than a criterion based on toxicologic endpoints. The 1980 AWQC National Guidelines emphasized that criteria derived for organoleptic endpoints are not based on toxicological information, have no direct relationship to adverse human health effects and, therefore, do not necessarily represent approximations of acceptable risk levels for humans.

[1]Throughout this document, the term "risk level" regarding a cancer assessment using linear approach refers to an upper-bound estimate of excess lifetime cancer risk.

1.4 RELATIONSHIP OF WATER QUALITY STANDARDS TO AWQC

Under Section 303(c) of the CWA, States have the primary responsibility for establishing water quality standards, defined under the Act as designated beneficial uses of a water segment and the water quality criteria necessary to support those uses. Additionally, Native American Tribes authorized to administer the water quality standards program under 40 CFR 131.8 establish water quality standards for waters within their jurisdictions. This statutory framework allows States and authorized Tribes to work with local communities to adopt appropriate designated uses and to adopt criteria to protect those designated uses. Section 303(c) provides for EPA review of water quality standards and for promulgation of a superseding Federal rule in cases where State or Tribal standards are not consistent with the applicable requirements of the CWA and the implementing Federal regulations, or where the Agency determines Federal standards are necessary to meet the requirements of the Act. Section 303(c)(2)(B) specifically requires States and authorized Tribes to adopt water quality criteria for toxics for which EPA has published criteria under Section 304(a) and for which the discharge or presence could reasonably be expected to interfere with the designated use adopted by the State or Tribe. In adopting such criteria, States and authorized Tribes must establish numerical values based on one of the following: (1) 304(a) criteria; (2) 304(a) criteria modified to reflect site-specific conditions; or, (3) other scientifically defensible methods. In addition, States and authorized Tribes can establish narrative criteria where numeric criteria cannot be determined.

It must be recognized that the Act uses the term "criteria" in two different ways. In Section 303(c), the term is part of the definition of a water quality standard. Specifically, a water quality standard is composed of designated uses and the criteria necessary to protect those uses. Thus, States and authorized Tribes are required to adopt regulations which contain legally enforceable criteria. However, in Section 304(a) the term criteria is used to describe the scientific information that EPA develops to be used as guidance by States, authorized Tribes and EPA when establishing water quality standards pursuant to 303(c). Thus, two distinct purposes are served by the 304(a) criteria. The first is as guidance to the States and authorized Tribes in the development and adoption of water quality criteria which will protect designated uses, and the second is as the basis for promulgation of a superseding Federal rule when such action is necessary.

1.5 NEED FOR THE AWQC METHODOLOGY REVISIONS

Since 1980, EPA risk assessment practices have evolved significantly in all of the major Methodology areas: that is, cancer and noncancer risk assessments, exposure assessments, and bioaccumulation. When the 1980 Methodology was developed, EPA had not yet developed formal cancer or noncancer risk assessment guidelines. Since then, EPA has published several risk assessment guidelines. In cancer risk assessment, there have been advances in the use of mode of action (MOA) information to support both the identification of potential human carcinogens and the selection of procedures to characterize risk at low, environmentally relevant exposure levels. EPA published *Proposed Guidelines for Carcinogen Risk Assessment* (USEPA, 1996a, hereafter the "1996 proposed cancer guidelines"). These guidelines presented revised procedures to quantify cancer risk at low doses, replacing the current default use of the LMS model. Following review by the Agency's Science Advisory Board (SAB), EPA published the

revised *Guidelines for Carcinogen Risk Assessment–Review Draft* in July 1999 (USEPA, 1999a, hereafter the "1999 draft revised cancer guidelines"). In noncancer risk assessment, the Agency is moving toward the use of the benchmark dose (BMD) and other dose-response approaches in place of the traditional NOAEL approach to estimate an RfD or Reference Concentration (RfC). *Guidelines for Mutagenicity Risk Assessment* were published in 1986 (USEPA, 1986b). In 1991, the Agency published *Guidelines for Developmental Toxicity Risk Assessment* (USEPA, 1991), and it issued *Guidelines for Reproductive Toxicity Risk Assessment* in 1996 (USEPA, 1996b). In 1998, EPA published final *Guidelines for Neurotoxicity Risk Assessment* (USEPA, 1998), and in 1999 it issued the draft *Guidance for Conducting Health Risk Assessment of Chemical Mixtures* (USEPA, 1999b).

In 1986, the Agency made available to the public the Integrated Risk Information System (IRIS). IRIS is a database that contains risk information on the cancer and noncancer effects of chemicals. The IRIS assessments are peer reviewed and represent EPA consensus positions across the Agency's program and regional offices.

New studies have addressed water consumption and fish tissue consumption. These studies provide a more current and comprehensive description of national, regional, and special-population consumption patterns that EPA has reflected in the 2000 Human Health Methodology. In addition, more formalized procedures are now available to account for human exposure from multiple sources when setting health goals such as AWQC that address only one exposure source. In 1986, the Agency published the *Total Exposure Assessment Methodology (TEAM) Study: Summary and Analysis, Volume I, Final Report* (USEPA, 1986c), which presents a process for conducting comprehensive evaluation of human exposures. In 1992, EPA published the revised *Guidelines for Exposure Assessment* (USEPA, 1992), which describe general concepts of exposure assessment, including definitions and associated units, and provide guidance on planning and conducting an exposure assessment. The *Exposure Factors Handbook* was updated in 1997 (USEPA, 1997a). Also in 1997, EPA developed *Guiding Principles for Monte Carlo Analysis* (USEPA, 1997b) and published its *Policy for Use of Probabilistic Analysis in Risk Assessment* (see http://www.epa.gov/ncea/mcpolicy.htm). The Monte Carlo guidance can be applied to exposure assessments and risk assessments. The Agency has recently developed the Relative Source Contribution (RSC) Policy for assessing total human exposure to a contaminant and apportioning the RfD among the media of concern, published for the first time in this Methodology.

The Agency has moved toward the use of a bioaccumulation factor (BAF) to reflect the uptake of a contaminant from all sources (e.g., ingestion, sediment) by fish and shellfish, rather than just from the water column as reflected by the use of a bioconcentration factor (BCF) in the 1980 Methodology. The Agency has also developed detailed procedures and guidelines for estimating BAF values.

Another reason for the 2000 Human Health Methodology is the need to bridge the gap between the differences in the risk assessment and risk management approaches used by EPA's Office of Water for the derivation of AWQC under the authority of the CWA and Maximum Contaminant Level Goals (MCLGs) under the Safe Drinking Water Act (SDWA). Three notable differences are the treatment of chemicals designated as Group C, possible human carcinogens

under the 1996 proposed cancer guidelines, the consideration of non-water sources of exposure when setting an AWQC or MCLG for a noncarcinogen, and cancer risk ranges. Those three differences are described in the three subsections below, respectively.

1.5.1 Group C Chemicals

Chemicals were typically classified as Group C–i.e., possible human carcinogens–under the existing (1986) EPA cancer classification scheme for any of the following reasons:

1) Carcinogenicity has been documented in only one test species and/or only one cancer bioassay and the results do not meet the requirements of "sufficient evidence."

2) Tumor response is of marginal statistical significance due to inadequate design or reporting.

3) Benign, but not malignant, tumors occur with an agent showing no response in a variety of short-term tests for mutagenicity.

4) There are responses of marginal statistical significance in a tissue known to have a high or variable background rate.

The 1986 *Guidelines for Carcinogen Risk Assessment* (hereafter the "1986 cancer guidelines") specifically recognized the need for flexibility with respect to quantifying the risk of Group C, possible human carcinogens. The 1986 cancer guidelines noted that agents judged to be in Group C, possible human carcinogens, may generally be regarded as suitable for quantitative risk assessment, but that case-by-case judgments may be made in this regard.

The EPA Office of Water has historically treated Group C chemicals differently under the CWA and the SDWA. It is important to note that the 1980 AWQC National Guidelines for setting AWQC under the CWA predated EPA's carcinogen classification system, which was proposed in 1984 (USEPA, 1984) and finalized in 1986 (USEPA, 1986a). The 1980 AWQC National Guidelines did not explicitly differentiate among agents with respect to the weight of evidence for characterizing them as likely to be carcinogenic to humans. For all pollutants judged as having adequate data for quantifying carcinogenic risk–including those now classified as Group C–AWQC were derived based on data on cancer incidence. In the1980 AWQC National Guidelines, EPA emphasized that the AWQC for carcinogens should state that the recommended concentration for maximum protection of human health is zero. At the same time, the criteria published for specific carcinogens presented water concentrations for these pollutants corresponding to individual lifetime excess cancer risk levels in the range of 10^{-7} to 10^{-5}.

In the development of national primary drinking water regulations under the SDWA, EPA is required to promulgate a health-based MCLG for each contaminant. The Agency policy has been to set the MCLG at zero for chemicals with strong evidence of carcinogenicity associated with exposure from water. For chemicals with limited evidence of carcinogenicity, including many Group C agents, the MCLG was usually obtained using an RfD based on the

pollutant's noncancer effects with the application of an additional uncertainty factor of 1 to 10 to account for carcinogenic potential of the chemical. If valid noncancer data for a Group C agent were not available to establish an RfD but adequate data are available to quantify the cancer risk, then the MCLG was based upon a nominal lifetime excess cancer risk in the range of 10^{-6} to10^{-5} (ranging from one case in a population of one million to one case in a population of one hundred thousand). Even in those cases where the RfD approach has been used for the derivation of the MCLG for a Group C agent, the drinking water concentrations associated with excess cancer risks in the range of 10^{-6} to 10^{-5} were also provided for comparison.

It should also be noted that EPA's pesticides program has applied both of the previously described methods for addressing Group C chemicals in actions taken under the Federal Insecticide, Fungicide, and Rodenticide Act (FIFRA) and finds both methods applicable on a case-by-case basis. Unlike the drinking water program, however, the pesticides program does not add an extra uncertainty factor to account for potential carcinogenicity when using the RfD approach.

In the 1999 draft revised cancer guidelines, there are no more alphanumeric categories. Instead, there will be longer narratives for hazard characterization that will use consistent descriptive terms when assessing cancer risk.

1.5.2 Consideration of Non-water Sources of Exposure

The 1980 AWQC National Guidelines recommended that contributions from non-water sources, namely air and non-fish dietary intake, be subtracted from the Acceptable Daily Intake (ADI), thus reducing the amount of the ADI "available" for water-related sources of intake. In practice, however, when calculating human health criteria, these other exposures were generally not considered because reliable data on these exposure pathways were not available. Consequently, the AWQC were usually derived such that drinking water and fish ingestion accounted for the entire ADI (now called RfD).

In the drinking water program, a similar "subtraction" method was used in the derivation of MCLGs proposed and promulgated in drinking water regulations through the mid-1980s. More recently, the drinking water program has used a "percentage" method in the derivation of MCLGs for noncarcinogens. In this approach, the percentage of total exposure typically accounted for by drinking water, referred to as the relative source contribution (RSC), is applied to the RfD to determine the maximum amount of the RfD "apportioned" to drinking water reflected by the MCLG value. In using this percentage procedure, the drinking water program also applies a ceiling level of 80 percent of the RfD and a floor level of 20 percent of the RfD. That is, the MCLG cannot account for more than 80 percent of the RfD, nor less than 20 percent of the RfD.

The drinking water program usually takes a conservative approach to public health by applying an RSC factor of 20 percent to the RfD when adequate exposure data do not exist, assuming that the major portion (80 percent) of the total exposure comes from other sources, such as diet.

In the 2000 Human Health Methodology, guidance for the routine consideration of non-water sources of exposure [both ingestion exposures (e.g., food) and exposures other than the oral route (e.g., inhalation)] is presented. The approach is called the Exposure Decision Tree. Relative source contribution estimates will be made by EPA using this approach, which allows for use of either the subtraction or percentage methods, depending on chemical-specific circumstances, within the 20 to 80 percent range described above.

1.5.3 Cancer Risk Ranges

In addition to the different risk assessment approaches discussed above for deriving AWQC and MCLGs for Group C agents, there have been different risk management approaches by the drinking water and surface water programs on lifetime excess risk values when setting health-based criteria for carcinogens. The surface water program has derived AWQC for carcinogens that generally corresponded to lifetime excess cancer risk levels of 10^{-7} to 10^{-5}. The drinking water program has set MCLGs for Group C agents based on a slightly less stringent risk range of 10^{-6} to 10^{-5}, while MCLGs for chemicals with strong evidence of carcinogenicity (that is, classified as Group A, known, or B probable, human carcinogen) are set at zero. The drinking water program is now following the principles of the 1999 draft revised cancer guidelines to determine the type of low-dose extrapolation based on mode of action.

It is also important to note that under the drinking water program, for those substances having an MCLG of zero, enforceable Maximum Contaminant Levels (MCLs) have generally been promulgated to correspond with cancer risk levels ranging from 10^{-6} to 10^{-4}. Unlike AWQC and MCLGs which are strictly health-based criteria, MCLs are developed with consideration given to the costs and technological feasibility of reducing contaminant levels in water to meet those standards.

With the 2000 Human Health Methodology, EPA will publish its national 304(a) water quality criteria at a 10^{-6} risk level, which EPA considers appropriate for the general population. EPA is increasing the degree of consistency between the drinking water and ambient water programs, given the somewhat different requirements of the CWA and SDWA.

1.6 OVERVIEW OF THE AWQC METHODOLOGY REVISIONS

The following equations for deriving AWQC include toxicological and exposure assessment parameters which are derived from scientific analysis, science policy, and risk management decisions. For example, values for parameters such as a field-measured BAF or a point of departure from an animal study [in the form of a lowest-observed-adverse-effect level (LOAEL)/no-observed -adverse-effect level (NOAEL)/lower 95 percent confidence limit on a dose associated with a 10 percent extra risk (LED_{10})] are empirically measured using scientific methods. By contrast, the decision to use animal effects as surrogates for human effects involves judgment on the part of the EPA (and similarly, by other agencies) as to the best practice to follow when human data are lacking. Such a decision is, therefore, a matter of science policy. The choice of default fish consumption rates for protection of a certain percentage (i.e., the 90th percentile) of the general population is clearly a risk management decision. In many cases, the Agency has selected parameter values using its best judgment regarding the overall protection afforded by the resulting AWQC when all parameters are combined. For a longer discussion of the differences between science, science policy, and risk management, please refer to Section 2 of this document. Section 2 also provides further details with regard to risk characterization for this Methodology, with emphasis placed on explaining the uncertainties in the overall risk assessment.

The generalized equations for deriving AWQC based on noncancer effects are:

Noncancer Effects[2]

$$AWQC = RfD \cdot RSC \cdot \left(\frac{BW}{DI + \sum_{i=2}^{4} (FI_i \cdot BAF_i)} \right) \qquad \text{(Equation 1-1)}$$

Cancer Effects: Nonlinear Low-Dose Extrapolation

$$AWQC = \frac{POD}{UF} \cdot RSC \cdot \left(\frac{BW}{DI + \sum_{i=2}^{4} (FI_i \cdot BAF_i)} \right) \qquad \text{(Equation 1-2)}$$

[2] Although appearing in this equation as a factor to be multiplied, the RSC can also be an amount subtracted. Refer to the explanation key below the equations.

Cancer Effects: Linear Low-Dose Extrapolation

$$AWQC = RSD \cdot \left(\frac{BW}{DI + \sum_{i=2}^{4} (FI_i \cdot BAF_i)} \right) \qquad \text{(Equation 1-3)}$$

where:

AWQC	=	Ambient Water Quality Criterion (mg/L)
RfD	=	Reference dose for noncancer effects (mg/kg-day)
POD	=	Point of departure for carcinogens based on a nonlinear low-dose extrapolation (mg/kg-day), usually a LOAEL, NOAEL, or LED_{10}
UF	=	Uncertainty Factor for carcinogens based on a nonlinear low-dose extrapolation (unitless)
RSD	=	Risk-specific dose for carcinogens based on a linear low-dose extrapolation (mg/kg-day) (dose associated with a target risk, such as 10^{-6})
RSC	=	Relative source contribution factor to account for non-water sources of exposure. (Not used for linear carcinogens.) May be either a percentage (multiplied) or amount subtracted, depending on whether multiple criteria are relevant to the chemical.
BW	=	Human body weight (default = 70 kg for adults)
DI	=	Drinking water intake (default = 2 L/day for adults)
FI_i	=	Fish intake at trophic level (TL) I (I = 2, 3, and 4) (defaults for total intake = 0.0175 kg/day for general adult population and sport anglers, and 0.1424 kg/day for subsistence fishers). Trophic level breakouts for the general adult population and sport anglers are: TL2 = 0.0038 kg/day; TL3 = 0.0080 kg/day; and TL4 = 0.0057 kg/day.
BAF_i	=	Bioaccumulation factor at trophic level I (I=2, 3 and 4), lipid normalized (L/kg)

For highly bioaccumulative chemicals where ingestion from water might be considered negligible, EPA is currently evaluating the feasibility of developing and implementing AWQCs that are expressed in terms of concentrations in tissues of aquatic organisms. Such tissue residue criteria might be used as an alternative to AWQCs which are expressed as concentrations in water, particularly in situations where AWQCs are at or below the practical limits for quantifying a chemical in water. Even though tissue residue criteria would not require the use of a BAF in their derivation, implementing such criteria would still require a mechanism for relating chemical loads and concentrations in water and sediment to concentrations in tissues of appropriate fish and shellfish (e.g., a BAF or bioaccumulation model). At this time, no revisions are planned to the Methodology to provide specific guidance on developing fish tissue-based water quality criteria. However, guidance may be provided in the future either as a separate document or integrated in a specific 304(a) water quality criteria document for a chemical that warrants such an approach.

AWQC for the protection of human health are designed to minimize the risk of adverse effects occurring to humans from chronic (lifetime) exposure to substances through the ingestion of drinking water and consumption of fish obtained from surface waters. The Agency is not recommending the development of additional water quality criteria similar to the "drinking water health advisories" that focus on acute or short-term effects; these are not seen as routinely having a meaningful role in the water quality criteria and standards program. However, as discussed below, there may be some instances where the consideration of acute or short-term toxicity and exposure in the derivation of AWQC is warranted.

Although the AWQC are based on chronic health effects data (both cancer and noncancer effects), the criteria are intended to also be protective against adverse effects that may reasonably be expected to occur as a result of elevated acute or short-term exposures. That is, through the use of conservative assumptions with respect to both toxicity and exposure parameters, the resulting AWQC should provide adequate protection not only for the general population over a lifetime of exposure, but also for special subpopulations who, because of high water- or fish-intake rates, or because of biological sensitivities, have an increased risk of receiving a dose that would elicit adverse effects. The Agency recognizes that there may be some cases where the AWQC based on chronic toxicity may not provide adequate protection for a subpopulation at special risk from shorter-term exposures. The Agency encourages States, Tribes, and others employing the 2000 Human Health Methodology to give consideration to such circumstances in deriving criteria to ensure that adequate protection is afforded to all identifiable subpopulations. (See Section 4.3, Factors Used in the AWQC Computation, for additional discussion of these subpopulations.)

The EPA is in the process of revising its cancer guidelines, including its descriptions of human carcinogenic potential. Once final guidelines are published, they will be the basis for assessment under this methodology. In the meanwhile, the 1986 guidelines are used and extended with principles discussed in EPA's 1999 *Guidelines for Carcinogen Risk Assessment - Review Draft* (hereafter "1999 draft revised cancer guidelines"). These principles arise from new science about cancer discovered in the last 15 years and from EPA policy of recent years supporting full characterization of hazard and risk both for the general population and potentially sensitive groups such as children. These principles are incorporated in recent and ongoing assessments such as the reassessment of dioxin, consistent with the 1986 guidelines. Until final guidelines are published, information is presented to describe risk under both the old guidelines and draft revisions. Dose-response assessment under the 1986 guidelines employs a linearized multistage model to extrapolate tumor dose-response observed in animal or human studies down to zero dose, zero extra risk. The dose-response assessment under EPA's 1999 draft revised cancer guidelines is a two-step process. In the first step, the response data are modeled in the range of empirical observation. Modeling in the observed range is done with biologically based or appropriate curve-fitting modeling. In the second step, extrapolation below the range of observation is accomplished by biologically based modeling if there are sufficient data or by a default procedure (linear, nonlinear, or both). A point of departure (POD) for extrapolation is estimated from modeling observed data. The lower 95 percent confidence limit on a dose associated with 10 percent extra risk (LED_{10}) is the standard POD for low-dose extrapolation. The linear default procedure is a straight line extrapolation to the origin (i.e., zero dose, zero extra risk) from the POD, which is the LED_{10} identified in the observable response

range. The result of this procedure is generally comparable (within 2-fold) to that of using a linearized multistage model under existing, 1986 guidelines. The linear low-dose extrapolation applies to agents that are best characterized by the assumption of linearity (e.g., direct DNA reactive mutagens) for their MOA. A linear approach would also be applied when inadequate or no information is available to explain the carcinogenic MOA; this is a science policy choice in the interest of public health. If it is determined that the MOA understanding fully supports a nonlinear extrapolation, the AWQC is derived using the nonlinear default which is based on a margin of exposure (MOE) analysis using the LED_{10} as the POD and applying uncertainty factors (UFs) to arrive at an acceptable MOE. There may be situations where it is appropriate to apply both the linear and nonlinear default procedures (e.g., for an agent that is both DNA reactive and active as a promoter at higher doses).

For substances that are carcinogenic, particularly those for which the MOA suggests nonlinearity at low doses, the Agency recommends that an integrated approach be taken in looking at cancer and noncancer effects. If one effect does not predominate, AWQC values should be determined for both carcinogenic and noncarcinogenic endpoints. The lower of the resulting values should be used for the AWQC.

When deriving AWQC for noncarcinogens and carcinogens based on a nonlinear low-dose extrapolation, a factor is included to account for other non-water exposure sources [both ingestion exposures (e.g., food) and exposures other than the oral route (e.g., inhalation)] so that the entire RfD, or POD/UF, is not apportioned to drinking water and fish consumption alone. Guidance is provided in the 2000 Human Health Methodology for determining the factor (i.e., the RSC) to be used for a particular chemical. The Agency is recommending the use of an Exposure Decision Tree procedure to support the determination of the appropriate RSC value for a given water contaminant. In the absence of data, the Agency intends to use 20 percent of the RfD (or POD/UF) as the default RSC in calculating 304(a) criteria or promulgating State or Tribal water quality standards under Section 303(c).

With AWQC derived for carcinogens based on a linear low-dose extrapolation, the Agency will publish recommended criteria values at a 10^{-6} risk level. States and authorized Tribes can always choose a more stringent risk level, such as 10^{-7}. EPA also believes that criteria based on a 10^{-5} risk level are acceptable for the general population as long as States and authorized Tribes ensure that the risk to more highly exposed subgroups (sportfishers or subsistence fishers) does not exceed the 10^{-4} level. Clarification on this risk management decision is provided in Section 2 of this document.

The default fish consumption value for the general adult population in the 2000 Human Health Methodology is 17.5 grams/day, which represents an estimate of the 90^{th} percentile consumption rate for the U.S. adult population based on the U.S. Department of Agriculture's (USDA's) Continuing Survey of Food Intake by Individuals (CSFII) 1994-96 data (USDA, 1998). EPA will use this default intake rate with future national 304(a) criteria derivations or revisions. This default value is chosen to be protective of the majority of the general population. However, States and authorized Tribes are urged to use a fish intake level derived from local data on fish consumption in place of this default value when deriving AWQC, ensuring that the fish intake level chosen is protective of highly exposed individuals in the population. EPA has

provided default values for States and authorized Tribes that do not have adequate information on local or regional consumption patterns, based on numerous studies that EPA has reviewed on sport anglers and subsistence fishers. EPA's defaults for these population groups are estimates of their average consumption. EPA recommends a default of 17.5 grams/day for sport anglers as an approximation of their average consumption and 142.4 grams/day for subsistence fishers, which falls within the range of averages for this group. Consumption rates for women of childbearing age and children younger than 14 are also provided to maximize protection in those cases where these subpopulations may be at greatest risk.

In the 2000 Human Health Methodology, criteria are derived using a BAF rather than a BCF. To derive the BAF, States and authorized Tribes may use EPA's Methodology or any method consistent with this Methodology. EPA's highest preference in developing BAFs are BAFs based on field-measured data from local/regional fish.

1.7 REFERENCES

NRC (National Research Council). 1977. *Drinking Water and Health*. Safe Drinking Water Committee. National Academy of Sciences, National Academy Press. Washington, DC.

USDA. 1998. U.S. Department of Agriculture. *1994–1996 Continuing Survey of Food Intakes by Individuals and 1994–1996 Diet and Health Knowledge Survey*. Agricultural Research Service, USDA. NTIS CD–ROM, accession number PB98–500457.

USEPA (U.S. Environmental Protection Agency). 1980. Guidelines and methodology used in the preparation of health effect assessment chapters of the consent decree water criteria documents. *Federal Register* 45: 79347, Appendix 3.

USEPA (U.S. Environmental Protection Agency). 1984. Proposed guidelines for carcinogen risk assessment. *Federal Register* 49:46294.

USEPA (U.S. Environmental Protection Agency). 1986a. Guidelines for carcinogen risk assessment. *Federal Register* 51:33992-34003.

USEPA (U.S. Environmental Protection Agency). 1986b. Guidelines for mutagenicity risk assessment. *Federal Register* 51:34006-34012.

USEPA (U.S. Environmental Protection Agency). 1986c. *Total Exposure Assessment Model (TEAM) Study: Summary and Analysis, Volume I. Final Report.* EPA/600/6-87/002a.

USEPA (U.S. Environmental Protection Agency). 1986d. Guidelines for exposure assessment. *Federal Register* 51:34042-34054.

USEPA (U.S. Environmental Protection Agency). 1991. Guidelines for developmental toxicity risk assessment. *Federal Register* 56:63789- 63826.

USEPA (U.S. Environmental Protection Agency). 1992. Guidelines for exposure assessment. *Federal Register* 57:22888-22938.

USEPA (U.S. Environmental Protection Agency). 1996a. Proposed guidelines for carcinogen risk assessment. *Federal Register* 61:17960-18011.

USEPA (U.S. Environmental Protection Agency). 1996b. Guidelines for reproductive toxicity risk assessment. *Federal Register* 61: 6274-56322.

USEPA (U.S. Environmental Protection Agency). 1997a. *Exposure Factors Handbook*. Office of Research and Development. Washington, DC. EPA/600/P-95/002Fa..

USEPA (U.S. Environmental Protection Agency). 1997b. *Guiding Principles for Monte Carlo Analysis*. Risk Assessment Forum. Washington, DC. EPA/630/R-97/001.

USEPA (U.S. Environmental Protection Agency). 1998. Guidelines for neurotoxicity risk assessment. *Federal Register* 63: 26926.

USEPA (U.S. Environmental Protection Agency). 1999a. *1999 Guidelines for Carcinogen Risk Assessment. Review Draft*. Office of Research and Development. Washington, DC. NCEA-F-0644.

USEPA (U.S. Environmental Protection Agency). 1999b. *Guidance for Conducting Health Risk Assessment of Chemical Mixtures*. Final Draft. Risk Assessment Forum Technical Panel. Washington, DC. EPA/NCEA-C-0148. September. Website: http://www.epa.gov/ncea/raf/rafpub.htm

USEPA (U.S. Environmental Protection Agency). 2000. *Methodology for Deriving Ambient Water Quality Criteria for the Protection of Human Health (2000). Technical Support Document Volume 1: Risk Assessment.* Office of Science and Technology, Office of Water. Washington, DC. EPA-822-B-00-005. August.

2. CLARIFICATIONS ON THE METHODOLOGY, RISK CHARACTERIZATION, AND OTHER ISSUES FOR DEVELOPING CRITERIA

2.1 IDENTIFYING THE POPULATION SUBGROUP THAT THE AWQC SHOULD PROTECT

Water quality criteria are derived to establish ambient concentrations of pollutants which, if not exceeded, will protect the general population from adverse health impacts from those pollutants due to consumption of aquatic organisms and water, including incidental water consumption related to recreational activities. For each pollutant, chronic criteria are derived to reflect long-term consumption of food and water. An important decision to make when setting AWQC is the choice of the particular population to protect. For instance, criteria could be set to protect those individuals who have average or "typical" exposures, or the criteria could be set so that they offer greater protection to those individuals who are more highly exposed. EPA has selected default parameter values that are representative of several defined populations: adults in the general population; sport (recreational) fishers; subsistence fishers; women of childbearing age (defined as ages 15-44); and children (up to the age of 14). In deciding on default parameter values, EPA is aware that multiple parameters are used in combination when calculating AWQC (e.g., intake rates and body weight). EPA describes the estimated population percentiles that are represented by each of the default exposure parameter values in Section 4.

EPA's national 304(a) criteria are usually derived to protect the majority of the general population from chronic adverse health effects. EPA has used a combination of median values, mean values, and percentile estimates for the parameter value defaults to calculate its national 304(a) criteria. EPA believes that its assumptions afford an overall level of protection targeted at the high end of the general population (i.e., the target population or the criteria-basis population). EPA also believes that this is reasonably conservative and appropriate to meet the goals of the CWA and the 304(a) criteria program. EPA considers that its target protection goal is satisfied if the population as a whole will be adequately protected by the human health criteria when the criteria are met in ambient water. However, associating the derived criteria with a specific population percentile is far more difficult, and such a quantitative descriptor typically requires detailed distributional exposure and dose information. EPA's *Guidelines For Exposure Assessment* (USEPA, 1992) describes the extreme difficulty in making accurate estimates of exposures and indicates that uncertainties at the more extreme ends of the distribution increase greatly. On quantifying population exposures/risks, the guidelines specifically state:

> *In practice, it is difficult even to establish an accurate mean health effect risk for a population. This is due to many complications, including uncertainties in using animal data for human dose-response relationships, nonlinearities in the dose-response curve, projecting incidence data from one group to another dissimilar group, etc. Although it has been common practice to estimate the number of cases of disease, especially cancer, for populations exposed to chemicals, it should be understood that these estimates are not meant to be accurate estimates of real (or actuarial) cases of disease. The estimate's value lies in framing*

hypothetical risk in an understandable way rather than in any literal interpretation of the term "cases."

Although it is not possible to subject the estimates to such a rigorous analysis (say, for example, to determine what criterion value provides protection of exactly the 90th percentile of the population), EPA believes that the combination of parameter value assumptions achieves its target goal, without being inordinately conservative. The standard assumptions made for the national 304(a) criteria are as follows. The assumed body weight value used is an arithmetic mean, as are the RSC intake estimates of other exposures (e.g., non-fish dietary), when data are available. The BAF component data (e.g., for lipid values, for particulate and dissolved organic carbon) are based on median (i.e., 50th percentile) values. The drinking water intake values are approximately 90th percentile estimates and fish intake values are 90th percentile estimates. EPA believes the use of these values will result in 304(a) criteria that are protective of a majority of the population; this is EPA's goal.

However, EPA also strongly believes that States and authorized Tribes should have the flexibility to develop criteria, on a site-specific basis, that provide additional protection appropriate for highly exposed populations. EPA is aware that exposure patterns in general, and fish consumption in particular, vary substantially. EPA understands that highly exposed populations may be widely distributed geographically throughout a given State or Tribal area. EPA recommends that priority be given to identifying and adequately protecting the most highly exposed population. Thus, if the State or Tribe determines that a highly exposed population is at greater risk and would not be adequately protected by criteria based on the general population, and by the national 304(a) criteria in particular, EPA recommends that the State or Tribe adopt more stringent criteria using alternative exposure assumptions.

EPA has provided recommended default intake rates for various population groups for State and Tribal consideration. EPA does not intend for these alternative default values to be prescriptive. EPA strongly emphasizes its preference that States and Tribes use local or regional data over EPA's defaults, if they so choose, as being more representative of their population groups of concern.

In the course of updating the 2000 Human Health Methodology, EPA received some questions regarding the population groups for which the criteria would be developed. EPA does not intend to derive multiple 304(a) criteria for all subpopulation groups for every chemical. As stated above, criteria that address chronic adverse health effects are most applicable to the CWA Section 304(a) criteria program and the chemicals evaluated for this program. If EPA determined that pregnant women/fetuses or young children were the target population (or criteria basis population) of a chemical's RfD or POD/UF, then the 304(a) criteria would be developed using exposure parameters for that subgroup. This would only be relevant for acute or subchronic toxicity situations. This does not conflict with the fact that chronic health effects potentially reflect a person's exposure during both childhood and adult years.

For RfD-based and POD/UF-based chemicals, EPA's policy is that, in general, the RfD (or POD/UF) should not be exceeded and the exposure assumptions used should reflect the population of concern. It is recommended that when a State or authorized Tribe sets a

waterbody-specific AWQC, they consider the populations most exposed via water and fish. EPA's policy on cancer risk management goals is discussed in Section 2.4.

Health Risks to Children

In recognition that children have a special vulnerability to many toxic substances, EPA's Administrator directed the Agency in 1995 to explicitly and consistently take into account environmental health risks to infants and children in all risk assessments, risk characterizations, and public health standards set for the United States. In April 1997, President Clinton signed Executive Order 13045 on the protection of children from environmental health risks, which assigned a high priority to addressing risks to children. In May 1997, EPA established the Office of Children's Health Protection to ensure the implementation of the President's Executive Order. EPA has increased efforts to ensure its guidance and regulations take into account risks to children. Circumstances where risks to children should be considered in the context of the 2000 Human Health Methodology are discussed in the Section 3.2, Noncancer Effects (in terms of developmental and reproductive toxicity) and in Section 4, Exposure (for appropriate exposure intake parameters).

Details on risk characterization and the guiding principles stated above are included in EPA's March 21, 1995 policy statement and the discussion of risk characterization (USEPA, 1995) and the 1999 *Guidelines for Carcinogen Risk Assessment. Review Draft* (USEPA, 1999a) and the *Reproductive and Toxicity Risk Assessment Guidelines* of 1996 (USEPA, 1996b).

2.2 SCIENCE, SCIENCE POLICY, AND RISK MANAGEMENT

An important part of risk characterization, as described later in Section 2.7, is to make risk assessments transparent. This means that conclusions drawn from the science are identified separately from policy judgments and risk management decisions, and that the use of default values or methods, as well as the use of assumptions in risk assessments, are clearly articulated. In this Methodology, EPA has attempted to separate scientific analysis from science policy and risk management decisions for clarity. This should allow States and Tribes (who are also prospective users of this Methodology) to understand the elements of the Methodology accurately and clearly, and to easily separate out the scientific decisions from the science policy and risk management decisions. This is important so that when questions are asked regarding the scientific merit, validity, or apparent stringency or leniency of AWQC, the implementer of the criteria can clearly explain what judgments were made to develop the criterion in question and to what degree these judgments were based on science, science policy, or risk management. To some extent this process will also be displayed in future AWQC documents.

When EPA speaks of science or scientific analysis, it is referring to the extraction of data from toxicological or exposure studies and surveys with a minimum of judgment being used to make inferences from the available evidence. For example, if EPA is describing a POD from an animal study (e.g., a LOAEL), this is usually determined as a lowest dose that produces an observable adverse effect. This would constitute a scientific determination. Judgments applying science policy, however, may enter this determination. For example, several scientists may differ in their opinion of what is adverse, and this in turn can influence the selection of a LOAEL

in a given study. The use of an animal study to predict effects in a human in the absence of human data is an inherent science policy decision. The selection of specific UFs when developing an RfD is another example of science policy. In any risk assessment, a number of decision points occur where risk to humans can only be inferred from the available evidence. Both scientific judgments and policy choices may be involved in selecting from among several possible inferences when conducting a risk assessment.

Risk management is the process of selecting the most appropriate guidance or regulatory actions by integrating the results of risk assessment with engineering data and with social, economic, and political concerns to reach a decision. In this Methodology, the choice of a default fish consumption rate which is protective of 90 percent of the general population is a risk management decision. The choice of an acceptable cancer risk by a State or Tribe is a risk management decision.

Many of the components in the 2000 Human Health Methodology are an amalgam of science, science policy, and/or risk management. For example, most of the default values chosen by EPA are based on examination of scientific data and application of either science policy or risk management. This includes the default assumption of 2 liters a day of drinking water; the assumption of 70 kilograms for an adult body weight; the use of default percent lipid and particulate organic carbon/dissolved organic carbon (POC/DOC) for developing national BAFs; the default fish consumption rates for the general population and sport and subsistence anglers; and the choice of a default cancer risk level. Some decisions are more grounded in science and science policy (such as the choice of default BAFs) and others are more obviously risk management decisions (such as the determination of default fish consumption rates and cancer risk levels). Throughout the 2000 Human Health Methodology, EPA has identified the kind of decision necessary to develop defaults and what the basis for the decision was. More details on the concepts of science analysis, science policy, risk management, and how they are introduced into risk assessments are included in *Risk Assessment in the Federal Government: Managing the Process* (NRC, 1983).

2.3 SETTING CRITERIA TO PROTECT AGAINST MULTIPLE EXPOSURES FROM MULTIPLE CHEMICALS (CUMULATIVE RISK)

EPA is very much aware of the complex issues and implications of cumulative risk and has endeavored to begin developing an overall approach at the Agency-wide level. Assuming that multiple exposures to multiple chemicals are additive is scientifically sound if they exhibit the same toxic endpoints and modes of action. There are numerous publications relevant to cumulative risk that can assist States and Tribes in understanding the complex issues associated with cumulative risk. These include the following:

- Durkin, P.R., R.C. Hertzberg, W. Stiteler, and M. Mumtaz. 1995. The identification and testing of interaction patterns. *Toxicol. Letters* 79:251-264.

- Hertzberg, R.C., G. Rice, and L.K. Teuschler. 1999. Methods for health risk assessment of combustion mixtures. In: *Hazardous Waste Incineration: Evaluating the Human*

Health and Environmental Risks. S. Roberts, C. Teaf and J. Bean, (eds). CRC Press LLC, Boca Raton, FL. Pp. 105-148.

- Rice, G., J. Swartout, E. Brady-Roberts, D. Reisman, K. Mahaffey, and B. Lyon. 1999. Characterization of risks posed by combustor emissions. *Drug and Chem. Tox.* 22:221-240.

- USEPA. 1999. *Guidance for Conducting Health Risk Assessment of Chemical Mixtures. Final Draft.* Risk Assessment Forum Technical Panel. Washington, DC. NCEA-C-0148. September. Web site: http://www.epa.gov/ncea/raf/rafpub.htm

- USEPA. 1998. *Methodology for Assessing Health Risks Associated with Multiple Pathways of Exposure to Combustor Emissions*. (Update to EPA/600/6-90/003 *Methodology for Assessing Health Risks Associated with Indirect Exposure to Combustor Emissions*). National Center for Environmental Assessment. Washington, DC. EPA-600-R-98-137. Website http://www.epa.gov/ncea/combust.htm

- USEPA. 1996. PCBs: *Cancer Dose-Response Assessment and Application to Environmental Mixtures*. National Center for Environmental Assessment. Washington, DC. EPA/600/P-96/001F.

- USEPA. 1993. *Review Draft Addendum to the Methodology for Assessing Health Risks Associated with Indirect Exposure to Combustor Emissions*. Office of Health and Environmental Assessment, Office of Research and Development. Washington, DC. EPA/600/AP-93/003. November.

- USEPA. 1993. *Provisional Guidance for Quantitative Risk Assessment of Polycyclic Aromatic Hydrocarbons*. Office of Research and Development. Washington, DC. EPA/600/R-93/089. July.

- USEPA. 1990. *Technical Support Document on Health Risk Assessment of Chemical Mixtures*. Office of Research and Development. Washington, DC. EPA/600/8/90/064. August.

- USEPA. 1989a. *Risk Assessment Guidance for Superfund. Vol. 1. Human Health Evaluation Manual (Part A).* Office of Emergency and Remedial Response. Washington, DC. EPA/540/1-89/002.

- USEPA. 1989b. *Interim Procedures for Estimating Risks Associated with Exposures to Mixtures of Chlorinated Dibenzo-p-Dioxins and -Dibenzofurans (CDDs and CDFs) and 1989 Update*. Risk Assessment Forum. Washington, DC. EPA/625/3-89/016. March.

The Agency's program offices are also engaged in on-going discussions of the great complexities, methodological challenges, data adequacy needs and other information gaps, as well as the science policy and risk management decisions that will need to be made, as they pursue developing a sound strategy and, eventually, specific guidance for addressing cumulative

risks. As a matter of internal policy, EPA is committed to refining the Methodology as advances in relevant aspects of the science improve, as part of the water quality criteria program.

2.4 CANCER RISK RANGE

For deriving 304(a) criteria or promulgating water quality criteria for States and Tribes under Section 303(c) based on the 2000 Human Health Methodology, EPA intends to use the 10^{-6} risk level, which the Agency believes reflects an appropriate risk for the general population. EPA's program office guidance and regulatory actions have evolved in recent years to target a 10^{-6} risk level as an appropriate risk for the general population. EPA has recently reviewed the policies and regulatory language of other Agency mandates (e.g., the Clean Air Act Amendments of 1990, the Food Quality Protection Act) and believes the target of a 10^{-6} risk level is consistent with Agency-wide practice.

EPA believes that both 10^{-6} and 10^{-5} may be acceptable for the general population and that highly exposed populations should not exceed a 10^{-4} risk level. States or Tribes that have adopted standards based on criteria at the 10^{-5} risk level can continue to do so, if the highly exposed groups would at least be protected at the 10^{-4} risk level. However, EPA is not automatically assuming that 10^{-5} will protect "the highest consumers" at the 10^{-4} risk level. Nor is EPA advocating that States and Tribes automatically set criteria based on assumptions for highly exposed population groups at the 10^{-4} risk level. The Agency is simply endeavoring to add that a specific determination should be made to ensure that highly exposed groups do not exceed a 10^{-4} risk level. EPA understands that fish consumption rates vary considerably, especially among subsistence populations, and it is such great variation among these population groups that may make either 10^{-6} or 10^{-5} protective of those groups at a 10^{-4} risk level. Therefore, depending on the consumption patterns in a given State or Tribal jurisdiction, a 10^{-6} or 10^{-5} risk level could be appropriate. In cases where fish consumption among highly exposed population groups is of a magnitude that a 10^{-4} risk level would be exceeded, a more protective risk level should be chosen. Such determinations should be made by the State or Tribal authorities and are subject to EPA's review and approval or disapproval under Section 303(c) of the CWA.

Adoption of a 10^{-6} or 10^{-5} risk level, both of which States and authorized Tribes have chosen in adopting water quality standards to date, represents a generally acceptable risk management decision, and EPA intends to continue providing this flexibility to States and Tribes. EPA believes that such State or Tribal decisions are consistent with Section 303(c) if the State or authorized Tribe has identified the most highly exposed subpopulation, has demonstrated that the chosen risk level is adequately protective of the most highly exposed subpopulation, and has completed all necessary public participation. States and authorized Tribes also have flexibility in how they demonstrate this protectiveness and obtain such information. A State or authorized Tribe may use existing information as well as collect new information in making this determination. In addition, if a State or authorized Tribe does not believe that the 10^{-6} risk level adequately protects the exposed subpopulations, water quality criteria based on a more stringent risk level may be adopted. This discretion includes combining the 10^{-6} risk level with fish consumption rates for highly exposed population groups.

It is important to understand that criteria for carcinogens are based on chosen risk levels that inherently reflect, in part, the exposure parameters used to derive those values. Therefore, changing the exposure parameters also changes the risk. Specifically, the incremental cancer risk levels are *relative*, meaning that any given criterion associated with a particular cancer risk level is also associated with specific exposure parameter assumptions (e.g., intake rates, body weights). When these exposure parameter values change, so does the relative risk. For a criterion derived on the basis of a cancer risk level of 10^{-6}, individuals consuming up to 10 times the assumed fish intake rate would not exceed a 10^{-5} risk level. Similarly, individuals consuming up to 100 times the assumed rate would not exceed a 10^{-4} risk level. Thus, for a criterion based on EPA's default fish intake rate (17.5 gm/day) and a risk level of 10^{-6}, those consuming a pound per day (i.e., 454 grams/day) would potentially experience between a 10^{-5} and a 10^{-4} risk level (closer to a 10^{-5} risk level). (Note: Fish consumers of up to 1,750 gm/day would not exceed the 10^{-4} risk level.) If a criterion were based on high-end intake rates and the relative risk of 10^{-6}, then an average fish consumer would be protected at a cancer risk level of approximately 10^{-8}. The point is that the risks for different population groups are not the same.

2.5 MICROBIOLOGICAL AMBIENT WATER QUALITY CRITERIA

Guidance for deriving microbiological AWQC is not a part of this Methodology. In 1986, EPA published *Ambient Water Quality Criteria for Bacteria - 1986* (USEPA, 1986a), which updated and revised bacteriological criteria previously published in 1976 in *Quality Criteria for Water* (USEPA, 1976). The inclusion of guidance for deriving microbiological AWQC was considered in the 1992 national workshop that initiated the effort to revise the 1980 Methodology and was recommended by the SAB in 1993. Since that time, however, efforts separate from these Methodology revisions have addressed microbiological AWQC concerns. The purpose of this section is to briefly describe EPA's current recommendations and activities.

EPA's *Ambient Water Quality Criteria for Bacteria - 1986* recommends the use of *Escherichia coli* and enterococci rather than fecal coliforms (USEPA, 1986a). EPA's criteria recommendations are:

- Fresh water: *E. coli* not to exceed 126/100 ml or enterococci not to exceed 33/100 ml; and

- Marine water: enterococci not to exceed 35/100 ml.

These criteria should be calculated as the geometric mean based on five equally spaced samples taken over a 30-day period.

In addition, EPA recommends that States adopt a single sample maximum, based on the expected frequency of use. No sample taken should exceed this value. EPA specifies appropriate single sample maximum values in the 1986 criteria document.

Current Activities and Plans for Future Work

EPA has identified development of microbial water quality criteria as part of its strategy to control waterborne microbial disease, by controlling pathogens in waterbodies and by protecting designated uses, such as recreation and public water supplies. The program fosters an integrated approach to protect both ground-water and surface water sources. EPA plans to conduct additional monitoring for *Cryptosporidium parvum* and *E. coli*, and determine action plans in accordance with the results of this monitoring.

EPA recommends no change at this time in the stringency of its bacterial criteria for recreational waters; existing criteria and methodologies from 1986 will still apply. The recommended methods for *E. coli* and enterococci have been improved. As outlined in the *Action Plan for Beaches and Recreational Waters* (Beach Action Plan, see below), the Agency plans to conduct national studies on improving indicators together with epidemiology studies for new criteria development (USEPA, 1999b). The Agency is also planning to establish improved temporal and spatial monitoring protocols.

In the Beach Action Plan, EPA identifies a multi-year strategy for monitoring recreational water quality and communicating public health risks associated with potentially pathogen-contaminated recreational rivers, lakes, and ocean beaches. It articulates the Agency's rationale and goals in addressing specific problems and integrates all associated program, policy, and research needs and directions. The Beach Action Plan also provides information on timing, products and lead organization for each activity. These include activities and products in the areas of program development, risk communication, water quality indicator research, modeling and monitoring research, and exposure and health effects research.

Recently, EPA approved new 24-hour *E. coli* and enterococcus tests for recreational waters that may be used as an alternative to the 48-hour test (USEPA, 1997). EPA anticipates proposing these methods for inclusion in the 40 CRF 136 in the Fall of 2000. EPA has also published a video with accompanying manual on the original and newer methods for enterococci and *E. coli* (USEPA, 2000).

As part of the Beach Action Plan, EPA made the following recommendations for further Agency study:

- Future criteria development should consider the risk of diseases other than gastroenteritis. EPA intends to consider and evaluate such water-related exposure routes as inhalation and dermal absorption when addressing microbial health effects. The nature and significance of other than the classical waterborne pathogens are to some degree tied to the particular type of waste sources.

- A new set of indicator organisms may need to be developed for tropical water if it is proven that the current fecal indicators can maintain viable cell populations in the soil and water for significant periods of time in uniform tropical conditions. Some potential alternative indicators to be fully explored are coliphage, other bacteriophage, and *Clostridium perfringens*.

- Because animal sources of pathogens of concern for human infection such as *Giardia lamblia*, *Cryptosporidium parvum*, and *Escherichia coli* 0157:H7 may be waterborne or washed into water and thus become a potential source for infection, they should not be ignored in risk assessment. A likely approach would be phylogenetic differentiation; that is, indicators that are specific to, or can discriminate among, animal sources.

- EPA intends to develop additional data on secondary infection routes and infection rates from prospective epidemiology studies and outbreaks from various types of exposure (e.g., shellfish consumption, drinking water, recreational exposure).

- EPA needs to improve sampling strategies for recreational water monitoring including consideration of rainfall and pollution events to trigger sampling.

2.6 RISK CHARACTERIZATION CONSIDERATIONS

On March 21, 1995, EPA's Administrator issued the *EPA Risk Characterization Policy and Guidance* (USEPA, 1995). This policy and guidance is intended to ensure that characterization information from each stage of a risk assessment is used in forming conclusions about risk and that this information is communicated from risk assessors to risk managers, and from EPA to the public. The policy also provides the basis for greater clarity, transparency, reasonableness, and consistency in risk assessments across EPA programs. The fundamental principles which form the basis for a risk characterization are as follows:

- Risk assessments should be transparent, in that the conclusions drawn from the science are identified separately from policy judgments, and the use of default values or methods and the use of assumptions in the risk assessment are clearly articulated.

- Risk characterizations should include a summary of the key issues and conclusions of each of the other components of the risk assessments, as well as describe the likelihood of harm. The summary should include a description of the overall strengths and limitations (including uncertainties) of the assessment and conclusions.

- Risk characterizations should be consistent in general format, but recognize the unique characteristics of each specific situation.

- Risk characterizations should include, at least in a qualitative sense, a discussion of how a specific risk and its context compares with similar risks. This may be accomplished by comparisons with other pollutants or situations on which the Agency has decided to act, or other situations with which the public may be familiar. The discussion should highlight the limitations of such comparisons.

- Risk characterization is a key component of risk communication, which is an interactive process involving exchange of information and expert opinion among individuals, groups, and institutions.

Additional guiding principles include:

- The risk characterization integrates the information from the hazard identification, dose-response, and exposure assessments, using a combination of qualitative information, quantitative information, and information regarding uncertainties.

- The risk characterization includes a discussion of uncertainty and variability in the risk assessment.

- Well-balanced risk characterizations present conclusions and information regarding the strengths and limitations of the assessment for other risk assessors, EPA decision-makers, and the public.

In developing the methodology presented here, EPA has closely followed the risk characterization guiding principles listed above. As States and Tribes adopt criteria using the 2000 Human Health Methodology, they are strongly encouraged to follow EPA's risk characterization guidance. There are a number of areas within the Methodology and criteria development process where risk characterization principles apply:

- Integration of cancer and noncancer assessments with exposure assessments, including bioaccumulation potential determinations, in essence, weighing the strengths and weaknesses of the risk assessment as a whole when developing a criterion.

- Selecting a fish consumption rate, either locally derived or the national default value, within the context of a target population (e.g., sensitive subpopulations) as compared to the general population.

- Presenting cancer and/or noncancer risk assessment options.

- Describing the uncertainty and variability in the hazard identification, the dose-response, and the exposure assessment.

2.7 DISCUSSION OF UNCERTAINTY

2.7.1 Observed Range of Toxicity Versus Range of Environmental Exposure

When characterizing a risk assessment, an important distinction to make is between the observed range of adverse effects (from an epidemiology or animal study) and the environmentally observed range of exposure (or anticipated human exposure) to the contaminant. In many cases, EPA intends to apply default factors to account for uncertainties or incomplete knowledge in developing RfDs or cancer risk assessments using nonlinear low-dose extrapolation to provide a margin of protection. In reality, the actual effect level and the environmental exposure levels may be separated by several orders of magnitude. The difference between the dose causing some observed response and the anticipated human exposure should be described by risk assessors and managers, especially when comparing criteria to environmental levels of a contaminant.

2.7.2 Continuum of Preferred Data/Use of Defaults

In both toxicological and exposure assessments, EPA has defined a continuum of preferred data for toxicological assessments ranging from a highest preference for chronic human data (e.g., studies that examine a long-term exposure of humans to a chemical, usually from occupational and/or residential exposure) and actual field data for many of the exposure parameter values (e.g., locally derived fish consumption rates, waterbody-specific bioaccumulation rates), to default values which are at the lower end of the preference continuum. EPA has supplied default values for all of the risk assessment parameters in the 2000 Human Health Methodology; however, it is important to note that when default values are used, the uncertainty in the final risk assessment may be higher, and the final resulting criterion may not be as applicable to local conditions, than is a risk assessment derived from human/field data. Using defaults assumes generalized conditions and may not capture the actual variability in the population (e.g., sensitive subpopulations/high-end consumers). If defaults are chosen as the basis for criteria, these inherent uncertainties should be communicated to the risk manager and the public. While this continuum is an expression of preference on the part of EPA, it does not imply in any way that any of the choices are unacceptable or scientifically indefensible.

2.7.3 Significant Figures

The number of significant figures in a numeric value is the number of certain digits plus one estimated digit. Digits should not be confused with decimal places. For example, 15.1, 0.0151, and 0.0150 all have 3 significant figures. Decimal places may have been used to maintain the correct number of significant figures, but in themselves they do not indicate significant figures (Brinker, 1984). Since the number of significant figures must include only one estimated digit, the sources of input parameters (e.g., fish consumption and water consumption rates) should be checked to determine the number of significant figures associated with data they provide. However, the original measured values may not be available to determine the number of significant figures in the input parameters. In these situations, EPA recommends utilizing the data as presented.

When developing criteria, EPA recommends rounding the number of significant figures at the end of the criterion calculation to the same number of significant figures in the least precise parameter. This is a generally accepted practice which can be found described in greater detail in APHA (1992) and Brinker (1984). The general rule is that for multiplication or division, the resulting value should not possess any more significant figures than is associated with the factor in the calculation with the least precision. When numbers are added or subtracted, the number that has the fewest decimal places, not necessarily the fewest significant figures, puts the limit on the number of places that justifiably may be carried in the sum or difference. Rounding off a number is the process of dropping one or more digits so that the value contains only those digits that are significant or necessary in subsequent computations (Brinker, 1984). The following rounding procedures are recommended: (1) if the digit 6, 7, 8, or 9 is dropped, increase the preceding digit by one unit; (2) if the digit 0, 1, 2, 3, or 4 is dropped, do not alter the preceding digit; and (3) if the digit 5 is dropped, round off the preceding digit to the nearest even number (e.g., 2.25 becomes 2.2 and 2.35 becomes 2.4) (APHA, 1992; Brinker, 1984).

EPA recommends that calculations of water quality criteria be performed without rounding of intermediate step values. The resulting criterion may be rounded to a manageable number of decimal places. However, in no case should the number of digits presented exceed the number of significant figures implied in the data and calculations performed on them. The term "intermediate step values" refers to values of the parameters in Equations 1-1 through 1-3. The final step is considered the resulting AWQC. Although AWQC are, in turn, used for purposes of establishing water quality-based effluent limits (WQBELs) in National Pollutant Discharge Elimination System (NPDES) permits, calculating total maximum daily loads (TMDLs), and applicable or relevant and appropriate requirements (ARARs) for Superfund, they are considered the final step of this Methodology and, for the purpose of this discussion, where the rounding should occur.

The determination of appropriate significant figures inevitably involves some judgment given that some of the equation parameters are adopted default exposure values. Specifically, the default drinking water intake rate of 2 L/day is a value adopted to represent a majority of the population over the course of a lifetime. Although supported by drinking water consumption survey data, this value was adopted as a policy decision and, as such, does not have to be considered in determining the parameter with the least precision. That is, the resulting AWQC need not always be reduced to one significant digit. Similarly, the 70-kg adult body weight has been adopted Agency-wide and represents a default policy decision.

The following example with a simplified AWQC equation illustrates the rule described above. The example is for hexachlorobutadiene (HCBD), which EPA used to demonstrate the 1998 draft Methodology revisions (USEPA, 1998b). The parameters that were calculated (i.e., not policy adopted values) include values with significant figures of two (the POD and RSC), three (the UF), and four (the FI and BAF). Based on the 2000 Human Health Methodology, the final criterion should be rounded to two significant figures. The bold numbers in parentheses indicate the number of significant figures and those with asterisks also indicate Agency adopted policy values.

$$AWQC = \frac{POD}{UF} \cdot RSC \cdot \left(\frac{BW}{DI + (FI \cdot BAF)} \right) \qquad \text{(Equation 2-1)}$$

Example [Refer to draft HCBD document for details on the POD/UF, RSC and BAF data (EPA 822-R-98-004). Also note that the fish intake rate in this example is the revised value.]:

$$AWQC = \left(\frac{0.054\mathbf{(2)}}{300\mathbf{(3)}} - 1.2 \times 10^{-4}\mathbf{(2)} \right) \times \left(\frac{70\mathbf{(2^*)}}{2\mathbf{(1^*)} + (0.01750\mathbf{(4)} \times 3{,}180\mathbf{(4)})} \right)$$

AWQC = 7.3×10^{-5} mg/L (0.073 µg/L, rounded from 7.285×10^{-2} µg/L)
* represents Agency adopted policy value

A number of the values used in the equation may result in intermediate step values that have more than four figures past the decimal place and may be carried throughout the calculation. However, carrying more than four figures past the decimal place (equivalent to the most precise parameter) is unnecessary as it has no effect on the resulting criterion value.

2.8 OTHER CONSIDERATIONS

2.8.1 Minimum Data Considerations

For many of the preceding technical areas, considerations have been presented for data quality in developing toxicological and exposure assessments. For greater detail and discussion of minimum data recommendations, the reader is referred to the specific sections in the Methodology on cancer and noncancer risk assessments (and especially to the referenced EPA risk assessment guidelines documents), exposure assessment, and bioaccumulation assessment, in addition to the TSD volumes for each.

2.8.2 Site-Specific Criterion Calculation

The 2000 Human Health Methodology allows for site-specific modifications by States and Tribes to reflect local environmental conditions and human exposure patterns. "Local" may refer to any appropriate geographic area where common aquatic environmental or exposure patterns exist. Thus "local" may signify Statewide, regional, a river reach, or an entire river.

Such site-specific criteria may be developed as long as the site-specific data, either toxicological or exposure-related, is justifiable. For example, when using a site-specific fish consumption rate, a State should use a value that represents at least the central tendency of the population surveyed (either sport or subsistence, or both). If a site-specific fish consumption rate for sport anglers or subsistence anglers is lower than an EPA default value, it may be used in calculating AWQC. However, to justify such a level (either higher or lower than EPA defaults), the State should assemble appropriate survey data to arrive at a defensible site-specific fish consumption rate.

Such data must also be submitted to EPA for its review when approving or disapproving State or Tribal water quality standards under Section 303(c). The same conditions apply to site-specific calculations of BAF, percent fish lipid, or the RSC. In the case of deviations from toxicological values (i.e., IRIS values: verified noncancer and cancer assessments), EPA strongly recommends that the data upon which the deviation is based be presented to and approved by the Agency before a criterion is developed.

Additional guidance on site-specific modifications to the 2000 Human Health Methodology is provided in each of the three TSD volumes.

2.8.3 Organoleptic Criteria

Organoleptic criteria define concentrations of chemicals or materials which impart undesirable taste and/or odor to water. Organoleptic effects, while significant from an aesthetic standpoint, are not a significant health concern. In developing and utilizing such criteria, two factors must be appreciated: (1) the limitations of most organoleptic data; and (2) the human health significance of organoleptic properties. In the past, EPA has developed organoleptic criteria if organoleptic data were available for a specific contaminant. The 1980 AWQC National Guidelines made a clear distinction that organoleptic criteria and toxicity-based criteria are derived from completely different endpoints, and that organoleptic criteria have no demonstrated relationship to potential adverse human health effects because there is no toxicological basis. EPA acknowledges that if organoleptic effects (i.e., objectionable taste and odor) cause people to reject the water and its designated uses, then the public is effectively deprived of the natural resource. It is also possible that intense organoleptic characteristics could result in depressed fluid intake which, in turn, might lead to an indirect human health effect via decreased fluid consumption. Although EPA has developed organoleptic criteria in the past and may potentially do so in the future, this will not be a significant part of the water quality criteria program. EPA encourages the development of organoleptic criteria when States and Tribes believe they are needed. However, EPA cautions States and Tribes that the quality of organoleptic data is often significantly less than that of toxicologic data used in establishing health-based criteria. Therefore, a comprehensive evaluation of available organoleptic data should be made, and the selection of the most appropriate database for the criterion should be based on sound scientific judgment.

In 1980, EPA provided recommended criteria summary language when both types of data are available. The following format was used and is repeated here:

> *For comparison purposes, two approaches were used to derive criterion levels for ____. Based on available toxicity data, for the protection of public health the derived level is ____. Using available organoleptic data, for controlling undesirable taste and odor quality of ambient water the estimated level is ____. It should be recognized that organoleptic data as a basis for establishing a water quality criteria have no demonstrated relationship to potential adverse human health effects.*

Similarly, the 1980 Methodology recommended that in those instances where a level to limit toxicity cannot be derived, the following statement should be provided:

> *Sufficient data are not available for ____ to derive a level which would protect against the potential toxicity of this compound.*

2.8.4 Criteria for Chemical Classes

The 2000 Human Health Methodology also allows for the development of a criterion for classes of chemicals, as long as a justification is provided through the analysis of mechanistic data, toxicokinetic data, structure-activity relationship data, and limited acute and chronic toxicity data. When potency differences between members of a class is great (such as in the case

of chlorinated dioxins and furans), toxicity equivalency factors (TEFs) may be more appropriately developed than one class criterion.

A chemical class is defined as any group of chemical compounds which are similar in chemical structure and biological activity, and which frequently occur together in the environment usually because they are generated by the same commercial process. In criterion development, isomers should be regarded as part of a chemical class rather than as a single compound. A class criterion, therefore, is an estimate of risk/safety which applies to more than one member of a class. It involves the use of available data on one or more chemicals of a class to derive criteria for other compounds of the same class in the event that there are insufficient data available to derive compound-specific criteria. The health-based criterion may apply to the water concentration of each member of the class, or may apply to the sum of the water concentrations of the compounds within the class. Because relatively minor structural changes within the class of compounds can have pronounced effects on their biological activities, reliance on class criteria should be minimized depending on the data available.

The following guidance should also be followed when considering the development of a class criterion.

- A detailed review of the chemical and physical properties of the chemicals within the group should be made. A close relationship within the class with respect to chemical activity would suggest a similar potential to reach common biological sites within tissues. Likewise, similar lipid solubilities would suggest the possibility of comparable absorption and distribution.

- Qualitative and quantitative toxicological data for chemicals within the group should be examined. Adequate toxicological data on a number of compounds within a group provides a more reasonable basis for extrapolation to other chemicals of the same class than minimal data on one chemical or a few chemicals within the group.

- Similarities in the nature of the toxicological response to chemicals in the class provides additional support for the prediction that the response to other members of the class may be similar. In contrast, where the biological response has been shown to differ markedly on a qualitative and quantitative basis for chemicals within a class, the extrapolation of a criterion to other members is not appropriate.

- Additional support for the validity of extrapolation of a criterion to other members of a class could be provided by evidence of similar metabolic and toxicokinetic data for some members of the class.

Additional guidance is described in the *Technical Support Document on Health Risk Assessment of Chemical Mixtures* (USEPA, 1990).

2.9.5 Criteria for Essential Elements

Developing criteria for essential elements, particularly metals, must be a balancing act between toxicity and the requirement for good health. The AWQC must consider essentiality and cannot be established at levels that would result in deficiency of the element in the human population. The difference between the recommended daily allowance (RDA) and the daily doses causing a specified risk level for carcinogens or the RfDs for noncarcinogens defines the spread of daily doses within which the criterion may be derived. Because errors are inherent in defining both essential and adverse-effect levels, the criterion is derived from a dose level near the center of such dose ranges.

The process for developing criteria for essential elements should be similar to that used for any other chemical with minor modifications. The RfD represents concern for one end of the exposure spectrum (toxicity), whereas the RDA represents the other end (minimum essentiality). While the RDA and RfD values might occasionally appear to be similar in magnitude to one another, it does not imply incompatibility of the two methodological approaches, nor does it imply inaccuracy or error in either calculation.

2.9 REFERENCES

APHA. American Public Health Association. 1992. *Standard Methods: For the Examination of Water and Wastewater*. 18th Edition. Prepared and published jointly by: American Public Health Association, American Water Works Association, and Water Environment Federation. Washington, DC.

Brinker, R.C. 1984. *Elementary Surveying.* 7th Edition. Cliff Robichaud and Robert Greiner, Eds. Harper and Row Publishers, Inc. New York, NY.

NRC (National Research Council). 1983. *Risk Assessment in the Federal Government: Managing the Process.* National Academy Press. Washington, DC.

USEPA (U.S. Environmental Protection Agency). 1976. *Quality Criteria for Water*. Office of Water and Hazardous Materials. Washington, DC. July.

USEPA (U.S. Environmental Protection Agency). 1986a. *Ambient Water Quality Criteria for Bacteria – 1986.* Office of Water Regulations and Standards. Washington, DC. EPA/440/5-84/002. January.

USEPA (U.S. Environmental Protection Agency). 1986b. *Test Methods for Escherichia coli and Enterococci in Water by the Membrane Filter Procedure*. Office of Research and Development. Cincinnati, OH. EPA/600/4-85/076.

USEPA (U.S. Environmental Protection Agency). 1990. *Technical Support Document on Health Risk Assessment of Chemical Mixtures*. Office of Research and Development. Washington, DC. EPA/600/8-90/064. August.

USEPA (U.S. Environmental Protection Agency). 1992. Guidelines for exposure assessment. *Federal Register* 57:22888-22938.

USEPA (U.S. Environmental Protection Agency). 1995. *Policy for Risk Characterization*. Memorandum of Carol M. Browner, Administrator. March 21, 1995. Washington, DC.

USEPA (U.S. Environmental Protection Agency). 1996a. Draft revisions to guidelines for carcinogen risk assessment. *Federal Register* 61:17960.

USEPA (U.S. Environmental Protection Agency). 1996b. Guidelines for reproductive toxicity risk assessment. *Federal Register* 61:6274-56322.

USEPA (U.S. Environmental Protection Agency). 1997. *Method 1600: Membrane Filter Test Method for Enterococci in Water*. Office of Water. Washington, DC. EPA/821/R-97/004. May.

USEPA (U.S. Environmental Protection Agency). 1998a. *Draft Water Quality Criteria Methodology: Human Health*. Office of Water. Washington, DC. EPA-822-Z-98-001. *(Federal Register* 63:43756)

USEPA (U.S. Environmental Protection Agency). 1998b. *Ambient Water Quality Criteria for the Protection of Human Health. Hexachlorobutadiene (HCBD). Draft*. Office of Water. Washington, DC. EPA 882-R-98-004. July.

USEPA (U.S. Environmental Protection Agency). 1999a. *1999 Guidelines for Carcinogen Risk Assessment. Review Draft*. Office of Research and Development. Washington, DC. NCEA-F-0644.

USEPA (U.S. Environmental Protection Agency). 1999b. *Action Plan for Beaches and Recreational Waters. Reducing Exposures to Waterborne Pathogens.* Office of Research and Development and Office of Water. Washington, DC. EPA-600-R-98-079. March.

USEPA (U.S. Environmental Protection Agency). 2000. *Improved Enumeration Methods for the Recreational Water Quality Indicators: Enterococci and Escherichia coli*. Office of Water, Office of Science and Technology. Washington, DC. EPA-821-R-97-004. March.

3. RISK ASSESSMENT

This section describes the methods used to estimate ambient water quality criteria (AWQC) for the protection of human health for carcinogenic chemicals (Section 3.1) and for noncarcinogenic chemicals (Section 3.2).

3.1 CANCER EFFECTS

3.1.1 Background on EPA Cancer Risk Assessment Guidelines

The current EPA *Guidelines for Carcinogen Risk Assessment* were published in 1986 (USEPA, 1986a, hereafter the "1986 cancer guidelines"). The 1986 cancer guidelines categorize chemicals into alpha-numerical Groups: A, known human carcinogen (sufficient evidence from epidemiological studies or other human studies); B, probable human carcinogen (sufficient evidence in animals and limited or inadequate evidence in humans); C, possible human carcinogen (limited evidence of carcinogenicity in animals in the absence of human data); D, not classifiable (inadequate or no animal evidence of carcinogenicity); and E, evidence of noncarcinogenicity for humans (no evidence of carcinogenicity in at least two adequate animal tests in different species or in both adequate epidemiological and animal studies). Within Group B there are two subgroups, Groups B1 and B2. Group B1 is reserved for agents for which there is limited evidence of carcinogenicity from epidemiological studies. Group B2 is generally for agents for which there is sufficient evidence from animal studies and for which there is inadequate evidence or no data from epidemiological studies (USEPA, 1986). The system was similar to that used by the International Agency for Research on Cancer (IARC).

The 1986 cancer guidelines include guidance on what constitutes sufficient, limited, or inadequate evidence. In epidemiological studies, sufficient evidence indicates a causal relationship between the agent and human cancer; limited evidence indicates that a causal relationship is credible, but that alternative explanations, such as chance, bias, or confounding, could not adequately be excluded; inadequate evidence indicates either lack of pertinent data, or a causal interpretation is not credible. In general, although a single study may be indicative of a cause-effect relationship, confidence in inferring a causal association is increased when several independent studies are concordant in showing the association. In animal studies, sufficient evidence includes an increased incidence of malignant tumors or combined malignant and benign tumors:

- In multiple species or strains;
- In multiple experiments (e.g., with different routes of administration or using different dose levels);
- To an unusual degree in a single experiment with regard to high incidence, unusual site or type of tumor, or early age at onset;
- Additional data on dose-response, short-term tests, or structural activity relationships.

In the 1986 cancer guidelines, hazard identification and the weight-of-evidence process focus on tumor findings. The weight-of-evidence approach for making judgments about cancer hazard analyzes human and animal tumor data separately, then combines them to make the overall conclusion about potential human carcinogenicity. The next step of the hazard analysis is an evaluation of supporting evidence (e.g., mutagenicity, cell transformation) to determine whether the overall weight-of-evidence conclusion should be modified.

For cancer risk quantification, the 1986 cancer guidelines recommend the use of linearized multistage model (LMS) as the only default approach. The 1986 cancer guidelines also mention that a low-dose extrapolation model other than the LMS might be considered more appropriate based on biological grounds. However, no guidance is given in choosing other approaches. The 1986 cancer guidelines recommended the use of body weight raised to the 2/3 power ($BW^{2/3}$) as a dose scaling factor between species.

3.1.2 EPA's Proposed Guidelines for Carcinogen Risk Assessment and the Subsequent July, 1999 Draft Revised Cancer Guidelines

In 1996, EPA published *Proposed Guidelines for Carcinogen Risk Assessment* (USEPA, 1996a, hereafter the "1996 proposed cancer guidelines"). After the publication of the 1996 proposed cancer guidelines and a February, 1997 and January, 1999 Science Advisory Board (SAB) review, a revision was made in July, 1999 *Guidelines for Carcinogen Risk Assessment - Review Draft* (hereafter the "1999 draft revised cancer guidelines"; USEPA, 1999a), and an SAB meeting was convened to review this revised document. When final guidelines are published, they will replace the 1986 cancer guidelines. These revisions are designed to ensure that the Agency's cancer risk assessment methods reflect the most current scientific information and advances in risk assessment methodology.

In the meanwhile, the 1986 guidelines are used and extended with principles discussed in the 1999 draft revised cancer guidelines. These principles arise from scientific discoveries concerning cancer made in the last 15 years and from EPA policy of recent years supporting full characterization of hazard and risk both for the general population and potentially sensitive groups such as children. These principles are incorporated in recent and ongoing assessments such as the reassessment of dioxin, consistent with the 1986 guidelines. Until final guidelines are published, information is presented to describe risk under both the 1986 guidelines and 1999 draft revisions.

The 1999 draft revised cancer guidelines call for the full use of all relevant information to convey the circumstances or conditions under which a particular hazard is expressed (e.g., route, duration, pattern, or magnitude of exposure). They emphasize understanding the mode of action (MOA) whereby the agent induces tumors. The MOA underlies the hazard assessment and provides the rationale for dose-response assessments.

The key principles in the 1999 draft revised cancer guidelines include:

a) Hazard assessment is based on the analysis of all biological information rather than just tumor findings.

b) An agent's MOA in causing tumors is emphasized to reduce the uncertainty in describing the likelihood of harm and in determining the dose-response approach(es).

c) The 1999 draft revised cancer guidelines emphasize the conditions under which the hazard may be expressed (e.g., route, pattern, duration and magnitude of exposure). Further, the guidelines call for a *hazard characterization* to integrate the data analysis of all relevant studies into a weight-of-evidence conclusion of hazard and to develop a working conclusion regarding the agent's mode of action in leading to tumor development.

d) A weight-of-evidence narrative with accompanying descriptors (listed in Section 3.1.3.1 below) would replace the current alphanumeric classification system. The narrative summarizes the key evidence for carcinogenicity, describes the agent's MOA, characterizes the conditions of hazard expression, including route of exposure, describes any disproportionate effects on subgroups of the human population (e.g., children), and recommends appropriate dose-response approach(es). Significant strengths, weaknesses, and uncertainties of contributing evidence are also highlighted.

e) Biologically based extrapolation models are the preferred approach for quantifying risk. These models integrate data and conclusions about events in the carcinogenic process throughout the dose-response range from high to low doses. It is anticipated, however, that the necessary data for the parameters used in such models will not be available for most chemicals. The 1999 draft revised cancer guidelines allow for alternative quantitative methods, including several default approaches.

f) Dose-response assessment is a two-step process. In the first step, response data are modeled in the observable range of data and a determination is made of the point of departure (POD) from the observed range to extrapolate to low doses. The second step is extrapolation from the POD to estimate dose-response at lower doses. In addition to modeling tumor data, the 1999 draft revised cancer guidelines call for the use and modeling of other kinds of responses if they are considered to be more informed measures of carcinogenic risk. Nominally, these responses reflect key events in the carcinogenic process integral to the MOA of the agent.

g) Three default approaches are provided–linear, nonlinear, or both when adequate data are unavailable to generate a biologically based model. As the first step for all approaches, curve fitting in the observed range is used to determine a POD. A standard POD is the effective dose corresponding to the lower 95 percent limit on

a dose associated with 10 percent extra risk (LED_{10}).[3] *Linear*: The linear default is a straight line extrapolation from the response at LED_{10} to the origin (zero dose, zero extra risk). *Nonlinear*: The nonlinear default begins with the identified POD and provides a margin of exposure (MOE) analysis rather than estimating the probability of effects at low doses. The MOE analysis is used to determine the appropriate margin between the POD and the exposure level of interest, in this Methodology, the AWQC. The key objective of the MOE analysis is to describe for the risk manager how rapidly responses may decline with dose. Other factors are also considered in the MOE analysis (i.e., nature of the response, slope of the dose-response curve, human sensitivity compared with experimental animals, nature and extent of human variability in sensitivity and human exposure). *Linear and nonlinear*: Section 3.1.3.4E describes the situations when both linear and nonlinear defaults are used.

h) The approach used to calculate an oral human equivalent dose when assessments are based on animal bioassays has been refined and includes a change in the default assumption for interspecies dose scaling. The 1999 draft revised cancer guidelines use body weight raised to the 3/4 power.

EPA health risk assessment practices for both cancer and noncancer endpoints are beginning to come together with recent proposals to emphasize MOA understanding in risk assessment and to model response data in the observable range to derive PODs for data sets and benchmark doses (BMDs) for individual studies. The modeling of observed response data to identify PODs in a standard way will help to harmonize cancer and noncancer dose-response approaches and permit comparisons of cancer and noncancer risk estimates.

3.1.3 Methodology for Deriving AWQC[4] by the 1999 Draft Revised Cancer Guidelines

Following the publication of the *Draft Water Quality Criteria Methodology: Human Health* (USEPA, 1998a) and the accompanying TSD (USEPA, 1998b), EPA received comments from the public. EPA also held an external peer review of the draft Methodology. Both the peer reviewers and the public recommended that EPA incorporate the new approaches into the AWQC Methodology.

Until new guidelines are published, the 1986 cancer guidelines will be used along with principles of the 1999 draft revised cancer guidelines. The 1986 guidelines are the basis for IRIS risk numbers which were used to derive the current AWQC. Each new assessment applying the principles of the 1999 draft revised cancer guidelines will be subject to peer review before being used as the basis of AWQC.

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[3] Use of the LED_{10} as the point of departure is recommended with this Methodology, as it is with the 1999 draft revised cancer guidelines.

[4] Additional information regarding the revised method for assessing carcinogens may be found in the *Methodology for Deriving Ambient Water Quality Criteria for the Protection of Human Health (2000). Technical Support Document, Volume 1: Risk Assessment* (USEPA, 2000).

The remainder of Section 3 illustrates the methodology for deriving numerical AWQC for carcinogens applying the 1999 draft revised cancer guidelines (USEPA, 1999a). This discussion of the revised methodology for carcinogens focuses primarily on the quantitative aspects of deriving numerical AWQC values. It is important to note that the cancer risk assessment process outlined in the 1999 draft revised cancer guidelines is not limited to the quantitative aspects. A numerical AWQC value derived for a carcinogen is to be based on appropriate hazard characterization and accompanied by risk characterization information.

This section contains a discussion of the weight-of-evidence narrative, that describes all information relevant to a cancer risk evaluation, followed by a discussion of the quantitative aspects of deriving numerical AWQC values for carcinogens. It is assumed that data from an appropriately conducted animal bioassay or human epidemiological study provide the underlying basis for deriving the AWQC value. The discussion focuses on the following: (1) the weight-of-evidence narrative; (2) general considerations and framework for analysis of the MOA; (3) dose estimation; (4) characterizing dose-response relationships in the range of observation and at low, environmentally relevant doses; (5) calculating the AWQC value; (6) risk characterization; and (7) use of Toxicity Equivalent Factors (TEF) and Relative Potency Estimates. The first three topics encompass the quantitative aspects of deriving AWQC for carcinogens.

3.1.3.1 Weight-of-Evidence Narrative[5]

The 1999 draft revised cancer guidelines include a weight-of-evidence narrative that is based on an overall judgment of biological and chemical/physical considerations. Hazard assessment information accompanying an AWQC value for a carcinogen in the form of a weight-of-evidence narrative is described in the footnote. Of particular importance is that the weight-of-evidence narrative explicitly provides adequate support based on human studies, animal bioassays, and other key evidence for the conclusion whether the substance is or is likely to be carcinogenic to humans from exposures through drinking water and/or fish ingestion. The Agency emphasizes the importance of providing an explicit discussion of the MOA for the substance in the weight-of-evidence narrative if data are available, including a discussion that relates the MOA to the quantitative procedures used in the derivation of the AWQC.

3.1.3.2 Mode of Action - General Considerations and Framework for Analysis

[5] The weight-of-evidence narrative is intended for the risk manager, and thus explains in nontechnical language the key data and conclusions, as well as the conditions for hazard expression. Conclusions about potential human carcinogenicity are presented by route of exposure. Contained within this narrative are simple likelihood descriptors that essentially distinguish whether there is enough evidence to make a projection about human hazard (i.e., Carcinogenic to humans; Likely to be carcinogenic to humans; Suggestive evidence of carcinogenicity but not sufficient to assess human carcinogenic potential; Data are inadequate for an assessment of human carcinogenic potential; and Not likely to be carcinogenic to humans). Because one encounters a variety of data sets on agents, these descriptors are not meant to stand alone; rather, the context of the weight-of-evidence narrative is intended to provide a transparent explanation of the biological evidence and how the conclusions were derived. Moreover, these descriptors should not be viewed as classification categories (like the alphameric system), which often obscure key scientific differences among chemicals. The new weight-of-evidence narrative also presents conclusions about how the agent induces tumors and the relevance of the mode of action to humans, and recommends a dose-response approach based on the MOA understanding (USEPA, 1996a, 1999a).

An MOA is composed of key events and processes starting with the interaction of an agent with a cell, through operational and anatomical changes, resulting in cancer formation. "Mode" of action is contrasted with "mechanism" of action, which implies a more detailed, molecular description of events than is meant by MOA.

Mode of action analysis is based on physical, chemical, and biological information that helps to explain key events[6] in an agent's influence on development of tumors. Inputs to MOA analysis include tumor data in humans, animals, and among structural analogues as well as the other key data.

There are many examples of possible modes of carcinogenic action, such as mutagenicity, mitogenesis, inhibition of cell death, cytotoxicity with reparative cell proliferation, and immune suppression. All pertinent studies are reviewed in analyzing an MOA, and an overall weighing of evidence is performed, laying out the strengths, weaknesses, and uncertainties of the case as well as potential alternative positions and rationales. Identifying data gaps and research needs is also part of the assessment.

Mode of action conclusions are used to address the question of human relevance of animal tumor responses, to address differences in anticipated response among humans such as between children and adults or men and women, and as the basis of decisions about the anticipated shape of the dose-response relationship.

In reaching conclusions, the question of "general acceptance" of an MOA will be tested as part of the independent peer review that EPA obtains for its assessment and conclusions.

Framework for Evaluating a Postulated Carcinogenic Mode(s) of Action

The framework is intended to be an analytic tool for judging whether available data support a mode of carcinogenic action postulated for an agent and includes nine elements:

1. Summary description of postulated MOA
2. Identification of key events
3. Strength, consistency, specificity of association
4. Dose-response relationship
5. Temporal relationship
6. Biological plausibility and coherence
7. Other modes of action
8. Conclusion
9. Human relevance, including subpopulations

3.1.3.3 Dose Estimation

[6]A "key event" is an empirically observable, precursor step that is itself a necessary element of the mode of action, or is a marker for such an element.

A. Determining the Human Equivalent Dose by the Oral Route

An important objective in the dose-response assessment is to use a measure of internal or delivered dose at the target site where possible. This is particularly important in those cases where the carcinogenic response information is being extrapolated to humans from animal studies. Generally, by the oral exposure route, the measure of a dose provided in the underlying human studies or animal bioassays is the applied dose, typically given in terms of unit mass per unit body weight per unit time, (e.g., mg/kg-day). When animal bioassay data are used, it is necessary to make adjustments to the applied dose values to account for differences in toxicokinetics between animals and humans that affect the relationship between applied dose and delivered dose at the target organ.

In the estimation of a human equivalent dose, the 1999 draft revised cancer guidelines recommend that when adequate data are available, the doses used in animal studies can be adjusted to equivalent human doses using toxicokinetic information on the particular agent. However, in most cases, there are insufficient data available to compare dose between species. In these cases, the estimate of a human equivalent dose is based on science policy default assumptions. To derive an equivalent human oral dose from animal data, the default procedure in the 1999 draft revised cancer guidelines is to scale daily applied oral doses experienced for a lifetime in proportion to body weight raised to the 3/4 power ($BW^{3/4}$). The adjustment factor is used because metabolic rates, as well as most rates of physiological processes that determine the disposition of dose, scale this way. Thus, the rationale for this factor rests on the empirical observation that rates of physiological processes consistently tend to maintain proportionality with body weight raised to 3/4 power (USEPA, 1992a, 1999a).

The use of $BW^{3/4}$ is a departure from the scaling factor of $BW^{2/3}$ that was based on surface area adjustment and was included in the 1980 AWQC National Guidelines as well as the 1986 cancer guidelines.

B. Dose-Response Analysis

If data on the agent are sufficient to support the parameters of a biologically based model and the purpose of the assessment is such as to justify investing resources supporting its use, this is the preferred approach for both the observed tumor and related response data and for extrapolation below the range of observed data in either animal or human studies.

3.1.3.4 Characterizing Dose-Response Relationships in the Range of Observation and at Low Environmentally Relevant Doses

The first quantitative component in the derivation of AWQC for carcinogens is the dose-response assessment in the range of observation. For most agents, in the absence of adequate data to generate a biologically based model, dose-response relationships in the observed range can be addressed through curve-fitting procedures for response data. It should be noted that the 1999 draft revised cancer guidelines call for modeling of not only tumor data in the observable range, but also other responses thought to be important events preceding tumor development (e.g., DNA adducts, cellular proliferation, receptor binding, hormonal changes). The modeling of

these data is intended to better inform the dose-response assessment by providing insights into the relationships of exposure (or dose) below the observable range for tumor response. These non-tumor response data can only play a role in the dose-response assessment if the agent's carcinogenic mode of action is reasonably understood, as well as the role of that precursor event.

The 1999 draft revised cancer guidelines recommend calculating the lower 95 percent confidence limit on a dose associated with an estimated 10 percent increased tumor or relevant non-tumor response (LED_{10}) for quantitative modeling of dose-response relationships in the observed range. The estimate of the LED_{10} is used as the POD for low-dose extrapolations discussed below. This standard point of departure (LED_{10}) is adopted as a matter of science policy to remain as consistent and comparable from case to case as possible. It is also a convenient comparison point for noncancer endpoints. The rationale supporting use of the LED_{10} is that a 10 percent response is at or just below the limit of sensitivity for discerning a statistically significant tumor response in most long-term rodent studies and is within the observed range for other toxicity studies. Use of lower limit takes experimental variability and sample size into account. The ED_{10} (central estimate) is also presented as a reference for comparison uses, especially for use in relative hazard/potency ranking among agents for priority setting.

For some data sets, a choice of the POD other than the LED_{10} may be appropriate. The objective is to determine the lowest reliable part of the dose-response curve for the beginning of the second step of the dose-response assessment—determine the extrapolation range. Therefore, if the observed response is below the LED_{10}, then a lower point may be a better choice (e.g., LED_5). Human studies more often support a lower POD than animal studies because of greater sample size.

The POD may be a NOAEL when a margin of exposure analysis is the nonlinear dose-response approach. The kinds of data available and the circumstances of the assessment both contribute to deciding to use a NOAEL or LOAEL which is not as rigorous or as ideal as curve fitting, but can be appropriate. If several data sets for key events and tumor response are available for an agent, and they are a mixture of continuous and incidence data, the most practicable way to assess them together is often through a NOAEL/LOAEL approach.

When an LED value estimated from animal data is used as the POD, it is adjusted to the human equivalent dose using an interspecies dose adjustment or a toxicokinetic analysis as described in Section 3.1.3.3.

Analysis of human studies in the observed range is designed on a case-by-case basis depending on the type of study and how dose and response are measured in the study.

A. Extrapolation to Low, Environmentally Relevant Doses

In most cases, the derivation of an AWQC will require an evaluation of carcinogenic risk at environmental exposure levels substantially lower than those used in the underlying study. Various approaches are used to extrapolate risk outside the range of observed experimental data. In the 1999 draft revised cancer guidelines, the choice of extrapolation method is largely

dependent on the mode of action. It should be noted that the term "mode of action" (MOA) is deliberately chosen in the 1999 draft revised cancer guidelines in lieu of the term "mechanism" to indicate using knowledge that is sufficient to draw a reasonable working conclusion without having to know the processes in detail as the term mechanism might imply. The 1999 draft revised cancer guidelines favor the choice of a biologically based model, if the parameters of such models can be calculated from data sources independent of tumor data. It is anticipated that the necessary data for such parameters will not be available for most chemicals. Thus, the 1999 draft revised cancer guidelines allow for several default extrapolation approaches (low-dose linear, nonlinear, or both).

B. Biologically Based Modeling Approaches

If a biologically based approach has been used to characterize the dose-response relationships in the observed range, and the confidence in the model is high, it may be used to extrapolate the dose-response relationship to environmentally relevant doses. For the purposes of deriving AWQC, the environmentally relevant dose would be the risk-specific dose (RSD) associated with incremental lifetime cancer risks in the 10^{-6} to 10^{-4} range for carcinogens for which a linear extrapolation approach is applied.[7] The use of the RSD and the POD/UF to compute the AWQC is presented in Section 3.1.3.5, below. Although biologically-based approaches are appropriate both for characterizing observed dose-response relationships and extrapolating to environmentally relevant doses, it is not expected that adequate data will be available to support the use of such approaches for most substances. In the absence of such data, the default linear approach, the nonlinear (MOE) approach, or both linear and nonlinear approaches will be used.

[7] For discussion of the cancer risk range, see Section 2.4.

C. Default Linear Extrapolation Approach

The default linear approach replaces the LMS approach that has served as the default for EPA cancer risk assessments. Any of the following conclusions leads to selection of a linear dose-response assessment approach:

- There is an absence of sufficient tumor MOA information.
- The chemical has direct DNA mutagenic reactivity or other indications of DNA effects that are consistent with linearity.
- Human exposure or body burden is high and near doses associated with key events in the carcinogenic process (e.g., 2,3,7,8-tetrachlorodibenzo-p-dioxin).
- Mode of action analysis does not support direct DNA effects, but the dose-response relationship is expected to be linear (e.g., certain receptor-mediated effects).

The procedures for implementing the default linear approach begin with the estimation of a POD as described above. The point of departure, LED_{10}, reflects the interspecies conversion to the human equivalent dose and the other adjustments for less-than-lifetime experimental duration. In most cases, the extrapolation for estimating response rates at low, environmentally relevant exposures is accomplished by drawing a straight line between the POD and the origin (i.e., zero dose, zero extra risk). This is mathematically represented as:

$$y = mx + b \qquad \text{(Equation 3-1)}$$
$$b = 0$$

where:

y	=	Response or incidence
m	=	Slope of the line (cancer potency factor) = $\Delta y/\Delta x$
x	=	Dose
b	=	Slope intercept

The slope of the line, "m" (the estimated cancer potency factor at low doses), is computed as:

$$m = \frac{0.10}{LED_{10}} \qquad \text{(Equation 3-2)}$$

The RSD is then calculated for a specific incremental targeted lifetime cancer risk (in the range of 10^{-6} to 10^{-4}) as:

$$RSD = \frac{\text{Target Incremental Cancer Risk}}{m} \qquad \text{(Equation 3-3)}$$

where:

RSD	=	Risk-specific dose (mg/kg-day)
Target Incremental Cancer Risk[8]	=	Value in the range of 10^{-6} to10^{-4}
m	=	Cancer potency factor $(mg/kg\text{-}day)^{-1}$

The use of the RSD to compute the AWQC is described in Section 3.1.3.5 below.

D. Default Nonlinear Approach

As discussed in the 1999 draft revised cancer guidelines, any of the following conclusions leads to a selection of a nonlinear (MOE) approach to dose-response assessment:

- A tumor MOA supporting nonlinearity applies (e.g., some cytotoxic and hormonal agents such as disruptors of hormonal homeostasis), and the chemical does not demonstrate mutagenic effects consistent with linearity.

- An MOA supporting nonlinearity has been demonstrated, and the chemical has some indication of mutagenic activity, but it is judged not to play a significant role in tumor causation.

Thus, a default assumption of nonlinearity is appropriate when there is no evidence for linearity and sufficient evidence to support an assumption of nonlinearity. The MOA may lead to a dose-response relationship that is nonlinear, with response falling much more quickly than linearly with dose, or being most influenced by individual differences in sensitivity. Alternatively, the MOA may theoretically have a threshold (e.g., the carcinogenicity may be a secondary effect of toxicity or of an induced physiological change that is itself a threshold phenomenon).

The nonlinear approach may be used, for instance, in the case of a bladder tumor inducer, where the chemical is not mutagenic and causes only stone formation in male rat bladders at high doses. This dynamic leads to tumor formation only at the high doses. Stone and subsequent tumor formation are not expected to occur at doses lower than those that induce the physiological changes that lead to stone formation. (More detail on this chemical is provided in the cancer section of the Risk Assessment TSD; USEPA, 2000). EPA does not generally try to distinguish between modes of action that might imply a “true threshold” from others with a

[8]In 1980, the target lifetime cancer risk range was set at 10-7 to 10-5. However, both the expert panel for the AWQC workshop (USEPA, 1993) and the peer review workshop experts (USEPA,1999c) recommended that EPA change the risk range to 10-6 to 10-4, to be consistent with SDWA program decisions. See Section 2.4 for more details.

nonlinear dose-response relationship, because there is usually not sufficient information to distinguish between those possibilities empirically.

The nonlinear MOE approach in the 1986 proposed cancer guidelines compares an observed response rate such as the LED_{10}, NOAEL, or LOAEL with actual or nominal environmental exposures of interest by computing the ratio between the two. In the context of deriving AWQC, the environmentally relevant exposures are nominal targets rather than actual exposures.

If the evidence for an agent indicates nonlinearity (e.g., when carcinogenicity is secondary to another toxicity for which there is a threshold), the MOE analysis for the toxicity is similar to what is done for a noncancer endpoint, and an RfD or RfC for that toxicity may also be estimated and considered in the cancer assessment. However, a threshold of carcinogenic response is not necessarily assumed. It should be noted that for cancer assessment, the MOE analysis begins from a POD that is adjusted for toxicokinetic differences between species to give a human equivalent dose.

To support the use of the MOE approach, risk assessment information provides evaluation of the current understanding of the phenomena that may be occurring as dose (exposure) decreases substantially below the observed data. This gives information about the risk reduction that is expected to accompany a lowering of exposure. The various factors that influence the selection of the UF in an MOE approach are also discussed below.

There are two main steps in the MOE approach. The first step is the selection of a POD. The POD may be the LED_{10} for tumor incidence or a precursor, or in some cases, it may also be appropriate to use a NOAEL or LOAEL value. When animal data are used, the POD is a human equivalent dose or concentration arrived at by interspecies dose adjustment (as discussed in Section 3.1.3.3) or toxicokinetic analysis.

The second step in using MOE analysis to establish AWQC is the selection of an appropriate margin or UF to apply to the POD. This is supported by analyses in the MOE discussion in the risk assessment. The following issues should be considered when establishing the overall UF for the derivation of AWQC using the MOE approach (others may be found appropriate in specific cases):

- The nature of the response used for the dose-response assessment, for instance, whether it is a precursor effect or a tumor response. The latter may support a greater MOE.

- The slope of the observed dose-response relationship at the POD and its uncertainties and implications for risk reduction associated with exposure reduction. (A steeper slope implies a greater reduction in risk as exposure decreases. This may support a smaller MOE).

- Human sensitivity compared with that of experimental animals.

- Nature and extent of human variability and sensitivity.

- Human exposure. The MOE evaluation also takes into account the magnitude, frequency, and duration of exposure. If the population exposed in a particular scenario is wholly or largely composed of a subpopulation of special concern (e.g., children) for whom evidence indicates a special sensitivity to the agent's MOA, an adequate MOE would be larger than for general population exposure.

E. Both Linear and Nonlinear Approaches

Any of the following conclusions leads to selection of both a linear and nonlinear approach to dose-response assessment. Relative support for each dose-response method and advice on the use of that information needs to be documented for the AWQC. In some cases, evidence for one MOA is stronger than for the other, allowing emphasis to be placed on that dose-response approach. In other cases, both modes of action are equally possible, and both dose-response approaches should be emphasized.

- Modes of action for a single tumor type support both linear and nonlinear dose response in different parts of the dose-response curve (e.g., 4,4' methylene chloride).

- A tumor mode of action supports different approaches at high and low doses; e.g., at high dose, nonlinearity, but, at low dose, linearity (e.g., formaldehyde).

- The agent is not DNA-reactive and all plausible modes of action are consistent with nonlinearity, but not fully established.

- Modes of action for different tumor types support differing approaches, e.g., nonlinear for one tumor type and linear for another due to lack of MOA information (e.g., trichloroethylene).

3.1.3.5 <u>AWQC Calculation</u>

A. Linear Approach

The following equation is used for the calculation of the AWQC for carcinogens where an RSD is obtained from the linear approach:

$$AWQC = RSD \cdot \left(\frac{BW}{DI + \sum_{i=2}^{4} (FI_i \cdot BAF_i)} \right) \qquad \text{(Equation 3-4)}$$

AWQC	=	Ambient water quality criterion (mg/L)
RSD	=	Risk-specific dose (mg/kg-day)
BW	=	Human body weight (kg)
DI	=	Drinking water intake (L/day)

FI_i	=	Fish intake at trophic level I (I = 2, 3, and 4) (kg/day)
BAF_i	=	Bioaccumulation factor for trophic level I (I = 2, 3, and 4), lipid normalized (L/kg)

B. Nonlinear Approach

In those cases where the nonlinear, MOE approach is used, a similar equation is used to calculate the AWQC [9]

$$AWQC = \frac{POD}{UF} \cdot RSC \cdot \left(\frac{BW}{DI + \sum_{i=2}^{4} (FI_i \cdot BAF_i)} \right) \qquad \text{(Equation 3-5)}$$

where variables are defined as for Equation 3-4 and:

POD	=	Point of departure (mg/kg-day)
UF	=	Uncertainty factor (unitless)
RSC	=	Relative source contribution (percentage or subtraction)

Differences between the AWQC values obtained using the linear and nonlinear approaches should be noted. First, the AWQC value obtained using the default linear approach corresponds to a specific estimated incremental lifetime cancer risk level in the range of 10^{-4} to 10^{-6}. In contrast, the AWQC obtained using the nonlinear approach does not describe a specific cancer risk. The AWQC calculations shown above are appropriate for waterbodies that are used as sources of drinking water.

The actual AWQC chosen for the protection of human health is based on a review of all relevant information, including cancer and noncancer data. The AWQC may, or may not, utilize the value obtained from the cancer analysis in the final AWQC value. The endpoint selected for the AWQC will be based on consideration of the weight of evidence and a complete analysis of all toxicity endpoints.

3.1.3.6 Risk Characterization

Risk assessment is an integrative process that is documented in a risk characterization summary. Risk characterization is the final step of the risk assessment process in which all preceding analyses (i.e., hazard, dose-response, and exposure assessments) are tied together to convey the overall conclusions about potential human risk. This component of the risk assessment process characterizes the data in nontechnical terms, explaining the extent and weight of evidence, major points of interpretation and rationale, and strengths and weaknesses of

[9] Although appearing in this equation as a factor to be multiplied, the RSC can also be an amount subtracted.

the evidence, and discussing alternative approaches, conclusions, uncertainties, and variability that deserve serious consideration.

Risk characterization information accompanies the numerical AWQC value and addresses the major strengths and weaknesses of the assessment arising from the availability of data and the current limits of understanding the process of cancer causation. Key issues relating to the confidence in the hazard assessment and the dose-response analysis (including the low-dose extrapolation procedure used) are discussed. Whenever more than one interpretation of the weight of evidence for carcinogenicity or the dose-response characterization can be supported, and when choosing among them is difficult, the alternative views are provided along with the rationale for the interpretation chosen in the derivation of the AWQC value. Where possible, quantitative uncertainty analyses of the data are provided; at a minimum, a qualitative discussion of the important uncertainties is presented.

3.1.3.7 Use of Toxicity Equivalence Factors and Relative Potency Estimates

The 1999 draft revised cancer guidelines state:

> *A toxicity equivalence factor (TEF) procedure is one used to derive quantitative dose-response estimates for agents that are members of a category or class of agents. TEFs are based on shared characteristics that can be used to order the class members by carcinogenic potency when cancer bioassay data are inadequate for this purpose. The ordering is by reference to the characteristics and potency of a well-studied member or members of the class. Other class members are indexed to the reference agent(s) by one or more shared characteristics to generate their TEFs.*

In addition, the 1999 draft revised cancer guidelines state that TEFs are generated and used for the limited purpose of assessment of agents or mixtures of agents in environmental media when better data are not available. When better data become available for an agent, the TEF should be replaced or revised. To date, adequate data to support use of TEFs have been found only for dibenzofurans (dioxins) and coplanar polychlorinated biphenyls (PCBs) (USEPA, 1989, 1999b).

The uncertainties associated with TEFs must be described when this approach is used. This is a default approach to be used when tumor data are not available for individual components in a mixture. Relative potency factors (RPFs) can be similarly derived and used for agents with carcinogenicity or other supporting data. The RPF is conceptually similar to TEFs, but does not have the same level of data to support it and thus has a less rigorous definition compared with the TEF. TEFs and RPFs are used only when there is no better alternative. When they are used, assumptions and uncertainties associated with them are discussed. As of today, there are only three classes of compounds for which relative potency approaches have been examined by EPA: dibenzofurans (dioxins), polychlorinated biphenyls (PCBs), and polycyclic aromatic hydrocarbons (PAHs). There are limitations to the use of TEF and RFP approaches, and caution should be exercised when using them. More guidance can be found in the draft document for conducting health risk assessment of chemical mixtures, published by the EPA Risk Assessment Forum (USEPA,1999b).

3.1.4 References for Cancer Section

Barnes, D.G., G.P Daston, J.S. Evans, A.M. Jarabek, R.J. Kavlock, C.A. Kimmel, C. Park, and H.L. Spitzer. 1995. Benchmark dose workshop: Criteria for use of a benchmark dose to estimate a reference dose. *Regul. Toxicol. Pharmacol*. 21:296-306.

USEPA (U.S. Environmental Protection Agency). 1980. Water quality criteria documents. *Federal Register* 45: 79318-79379.

USEPA (U.S. Environmental Protection Agency). 1986. Guidelines for carcinogen risk assessment. *Federal Register* 51:33992-34003.

USEPA (U.S. Environmental Protection Agency). 1989. *Interim Procedures for Estimating Risks Associated with Exposures to Mixtures of Chlorinated Dibenzo-p-dioxins and -Dibenzofurans (CDDs and CDFs) and 1989 Update*. Risk Assessment Forum. Washington, DC. EPA/625/3-89/016.

USEPA (U.S. Environmental Protection Agency). 1992a. Draft report: a cross-species scaling factor for carcinogen risk assessment based on equivalence of $mg/kg^{3/4}$/day. *Federal Register* 57: 24152-24173.

USEPA (U.S. Environmental Protection Agency). 1993. *Revision of Methodology for Deriving National Ambient Water Quality Criteria for the Protection of Human Health: Report of Workshop and EPA's Preliminary Recommendations for Revision.* Submitted to EPA Science Advisory Board Drinking Water Committee, January 8, 1993. Office of Science and Technology, Office of Water. Water Docket W-97-20.

USEPA (U.S. Environmental Protection Agency). 1996. *Proposed Guidelines for Carcinogen Risk Assessment.* Office of Research and Development. Washington, DC. EPA/600/P-92/003C. (*Federal Register* 61:17960)

USEPA (U.S. Environmental Protection Agency). 1998a. *Draft Water Quality Criteria Methodology: Human Health. Federal Register Notice*. Office of Water. Washington, DC. EPA-822-Z-98-001.

USEPA (U.S. Environmental Protection Agency). 1998b. *Ambient Water Quality Criteria Derivation Methodology - Human Health. Technical Support Document. Final Draft.* Office of Water. Washington, DC. EPA-822-B-98-005.

USEPA (U.S. Environmental Protection Agency). 1999a. *Guidelines for Carcinogen Risk Assessment. Review Draft*. Risk Assessment Forum. Washington, DC. EPA/NCEA-F-0644. July.

USEPA (U.S. Environmental Protection Agency). 1999b. *Guidance for Conducting Health Risk Assessment of Chemical Mixtures. External Peer Review Draft*. Risk Assessment Forum. Washington, DC. EPA/NCEA-C-0148. April.

USEPA (U.S. Environmental Protection Agency). 1999c. *Revisions to the Methodology for Deriving Ambient Water Quality Criteria for the Protection of Human Health. Peer Review Workshop Summary Report*. Office of Water. Washington, DC. EPA-822-R-99-015. September.

USEPA (U.S. Environmental Protection Agency). 2000. *Methodology for Deriving Ambient Water Quality Criteria for the Protection of Human Health (2000). Technical Support Document Volume 1: Risk Assessment.* Office of Science and Technology, Office of Water. Washington, DC. EPA-822-B-00-005. August.

3.2 NONCANCER EFFECTS

3.2.1 1980 AWQC National Guidelines for Noncancer Effects

In the 1980 AWQC National Guidelines, the Agency evaluated noncancer human health effects from exposure to chemical contaminants using Acceptable Daily Intake (ADI) levels. ADIs were calculated by dividing NOAELs by safety factors (SFs) to obtain estimates of doses of chemicals that would not be expected to cause adverse effects over a lifetime of exposure. In accordance with the National Research Council report of 1977 (NRC, 1977), EPA used SFs of 10, 100, or 1,000, depending on the quality and quantity of the overall database. In general, a factor of 10 was suggested when good-quality data identifying a NOAEL from human studies were available. A factor of 100 was suggested if no human data were available, but the database contained valid chronic animal data. For chemicals with no human data and scant animal data, a factor of 1,000 was recommended. Intermediate SFs could also be used for databases that fell between these categories.

AWQC were calculated using the ADI levels together with standard exposure assumptions about the rates of human ingestion of water and fish, and also accounting for intake from other sources (see Equation 1-1 in the Introduction). Surface water concentrations at or below the calculated criteria concentrations would be expected to result in human exposure levels at or below the ADI. Inherent in these calculations is the assumption that, generally, adverse effects from noncarcinogens exhibit a threshold.

3.2.2 Noncancer Risk Assessment Developments Since 1980

Since 1980, the risk assessment of noncarcinogenic chemicals has changed. To remove the value judgments implied by the words “acceptable” and “safety,” the ADI and SF terms have been replaced with the terms RfD and UF/modifying factor (MF), respectively.

For the risk assessment of general systemic toxicity, the Agency currently uses the guidelines contained in the IRIS background document entitled *Reference Dose (RfD): Description and Use in Health Risk Assessments* (hereafter the “IRIS background document”. That document defines an RfD as “an estimate (with uncertainty spanning approximately an order of magnitude) of a daily exposure to the human population (including sensitive subgroups) that is likely to be without appreciable risk of deleterious effects over a lifetime” (USEPA,

1993a). The most common approach for deriving the RfD does not involve dose-response modeling. Instead, an RfD for a given chemical is usually derived by first identifying the NOAEL for the most sensitive known toxicity endpoint, that is, the toxic effect that occurs at the lowest dose. This effect is called the critical effect. Factors such as the study protocol, the species of experimental animal, the nature of the toxicity endpoint assessed and its relevance to human effects, the route of exposure, and exposure duration are critically evaluated in order to select the most appropriate NOAEL from among all available studies in the chemical's database. If no appropriate NOAEL can be identified from any study, then the LOAEL for the critical effect endpoint is used and an uncertainly factor for LOAEL-to-NOAEL extrapolation is applied. Using this approach, the RfD is equal to the NOAEL (or LOAEL) divided by the product of UFs and, occasionally, an MF:

$$\text{RfD (mg/kg/day)} = \frac{\text{NOAEL (or LOAEL)}}{\text{UF} \cdot \text{MF}} \qquad \text{(Equation 3-6)}$$

The definitions and guidance for use of the UFs and the MFs are provided in the IRIS background document and are repeated in Table 3-1.

The IRIS background document on the RfD (USEPA, 1993a) provides guidance for critically assessing noncarcinogenic effects of chemicals and for deriving the RfD. Another reference on this topic is Dourson (1994). Furthermore, the Agency has also published separate guidelines for assessing specific toxic endpoints, such as developmental toxicity (USEPA, 1991a), reproductive toxicity (USEPA, 1996a), and neurotoxicity risk assessment (USEPA, 1995). These endpoint-specific guidelines will be used for their respective areas in the hazard assessment step and will complement the overall toxicological assessment. It should be noted, however, that an RfD, derived using the most sensitive known endpoint, is considered protective against all noncarcinogenic effects.

TABLE 3-1. UNCERTAINTY FACTORS AND THE MODIFYING FACTOR

Uncertainty Factor	Definition
UF_H	Use a 1, 3, or 10-fold factor when extrapolating from valid data in studies using long-term exposure to average healthy humans. This factor is intended to account for the variation in sensitivity (intraspecies variation) among the members of the human population.
UF_A	Use an additional factor of 1, 3, or 10 when extrapolating from valid results of long-term studies on experimental animals when results of studies of human exposure are not available or are inadequate. This factor is intended to account for the uncertainty involved in extrapolating from animal data to humans (interspecies variation).
UF_S	Use an additional factor of 1, 3, or 10 when extrapolating from less-than-chronic results on experimental animals when there are no useful long-term human data. This factor is intended to account for the uncertainty involved in extrapolating from less-than-chronic NOAELs to chronic NOAELs.
UF_L	Use an additional factor of 1, 3, or 10 when deriving an RfD from a LOAEL, instead of a NOAEL. This factor is intended to account for the uncertainty involved in extrapolating from LOAELs to NOAELs.
UF_D	Use an additional 3- or 10-fold factor when deriving an RfD from an "incomplete" database. This factor is meant to account for the inability of any single type of study to consider all toxic endpoints. The intermediate factor of 3 (approximately ½ $\log_{10}$ unit, i.e., the square root of 10) is often used when there is a single data gap exclusive of chronic data. It is often designated as UF_D.

Modifying Factor

Use professional judgment to determine the MF, which is an additional uncertainty factor that is greater than zero and less than or equal to 10. The magnitude of the MF depends upon the professional assessment of scientific uncertainties of the study and database not explicitly treated above (e.g., the number of species tested). The default value for the MF is 1.

Note: With each UF or MF assignment, it is recognized that professional scientific judgment must be used. The total product of the uncertainty factors and modifying factor should not exceed 3,000.

Similar to the procedure used in the 1980 AWQC National Guidelines, the revised method of deriving AWQC for noncarcinogens uses the RfD together with various assumptions concerning intake of the contaminant from both water and non-water sources of exposure. The objective of an AWQC for noncarcinogens is to ensure that human exposure to a substance related to its presence in surface water, combined with exposure from other sources, does not exceed the RfD. The algorithm for deriving AWQC for noncarcinogens using the RfD is presented as Equation 1-1 in the Introduction.

3.2.3 Issues and Recommendations Concerning the Derivation of AWQC for Noncarcinogens

During a review of the 1980 AWQC National Guidelines (USEPA, 1993b), the Agency identified several issues that must be resolved in order to develop a final revised methodology for deriving AWQC based on noncancer effects. These issues, as discussed below, mainly concern the derivation of the RfD as the basis for such an AWQC. Foremost among these issues is whether the Agency should revise the present method or adopt entirely new procedures that use quantitative dose-response modeling for the derivation of the RfD. Other issues include the following:

- Presenting the RfD as a single point value or as a range to reflect the inherent imprecision of the RfD;
- Selecting specific guidance documents for derivation of noncancer health effect levels;
- Considering severity of effect in the development of the RfD;
- Using less-than-90-day studies as the basis for RfDs;
- Integrating reproductive/developmental, immunotoxicity, and neurotoxicity data into the RfD calculation;
- Applying toxicokinetic data in risk assessments; and
- Considering the possibility that some noncarcinogenic effects do not exhibit a threshold.

3.2.3.1 Using the Current NOAEL/UF-Based RfD Approach or Adopting More Quantitative Approaches for Noncancer Risk Assessment

The current NOAEL/UF-based RfD methodology, or its predecessor ADI/SF methodology, have been used since 1980. This approach assumes that there is a threshold exposure below which adverse noncancer health effects are not expected to occur. Exposures above this threshold are believed to pose some risk to exposed individuals; however, the current approach does not address the nature and magnitude of the risk above the threshold level (i.e., the shape of the dose-response curve above the threshold). The NOAEL/UF-based RfD approach is intended primarily to ensure that the RfD value derived from the available data falls below the population effects threshold. However, the NOAEL/UF-based RfD procedure has

limitations. In particular, this method requires that one of the actual experimental doses used by the researchers in the critical study be selected as the NOAEL or LOAEL value. The determination that a dose is a NOAEL or LOAEL will depend on the biological endpoints used and the statistical significance of the data. Statistical significance will depend on the number and spacing of dose groups and the numbers of animals used in each dose group. Studies using a small number of animals can limit the ability to distinguish statistically significant differences among measurable responses seen in dose groups and control groups. Furthermore, the determination of the NOAEL or LOAEL also depends on the dose spacing of the study. Doses are often widely spaced, typically differing by factors of three to ten. A study can identify a NOAEL and a LOAEL from among the doses studied, but the "true" effects threshold cannot be determined from those results. The study size and dose spacing limitations also limit the ability to characterize the nature of the expected response to exposures between the observed NOAEL and LOAEL values.

The limitations of the NOAEL/UF approach have prompted development of alternative approaches that incorporate more quantitative dose-response information. The traditional NOAEL approach for noncancer risk assessment has often been a source of controversy and has been criticized in several ways. For example, experiments involving fewer animals tend to produce higher NOAELs and, as a consequence, may produce higher RfDs. Larger sample sizes, on the other hand, should provide greater experimental sensitivity and lower NOAELs. The focus of the NOAEL approach is only on the dose that is the NOAEL, and the NOAEL must be one of the experimental doses. It also ignores the shape of the dose-response curve. Thus, the slope of the dose-response plays little role in determining acceptable exposures for human beings. Therefore, in addition to the NOAEL/UF-based RfD approach described above, EPA will accept other approaches that incorporate more quantitative dose-response information in appropriate situations for the evaluation of noncancer effects and the derivation of RfDs. However, the Agency wishes to emphasize that it still believes the NOAEL/UF RfD methodology is valid and can continue to be used to develop RfDs.

Two alternative approaches that may have relevance in assisting in the derivation of the RfD for a chemical are the BMD and the categorical regression approaches. These alternative approaches may overcome some of the inherent limitations in the NOAEL/UF approach. For example, the BMD analyses for developmental effects show that NOAELs from studies correlate well with a 5 percent response level (Allen et al., 1994). The BMD and the categorical regression approaches usually have greater data requirements than the RfD approach. Thus, it is unlikely that any one approach will apply to every circumstance; in some cases, different approaches may be needed to accommodate the varying databases for the range of chemicals for which water quality criteria must be developed. Acceptable approaches will satisfy the following criteria: (1) meet the appropriate risk assessment goal; (2) adequately describe the toxicity database and its quality; (3) characterize the endpoints properly; (4) provide a measure of the quality of the "fit" of the model when a model is used for dose-response analysis; and (5) describe the key assumptions and uncertainties.

A. The Benchmark Dose

The BMD is defined as the dose estimated to produce a predetermined level of change in response (the Benchmark Response level, or BMR) relative to control. The BMDL is defined as the statistical lower confidence limit on the BMD. In the derivation of an RfD, the BMDL is used as the dose to which uncertainty factors are applied instead of the NOAEL. The BMD approach first models a dose-response curve for the critical effect(s) using available experimental data. Several mathematical algorithms can be used to model the dose-response curve, such as polynomial or Weibull functions. To define a BMD from the modeled curve for quantal data, the assessor first selects the BMR. The choice of the BMR is critical. For quantal endpoints, a particular level of response is chosen (e.g., 1 percent, 5 percent, or 10 percent). For continuous endpoints, the BMR is the degree of change from controls and is based on what is considered a biologically significant change. The BMD is derived from the BMR dose by applying the desired confidence limit calculation. The RfD is obtained by dividing the BMD by one or more uncertainty factors, similar to the NOAEL approach. Because the BMD is used like the NOAEL to obtain the RfD, the BMR should be selected at or near the low end of the range of increased risks that can be detected in a study of typical size. Generally, this falls in the range between the ED_{01} and the ED_{10}.

The Agency will accept use of a BMD approach to derive RfDs for those agents for which there is an adequate database. There are a number of technical decisions associated with the application of the BMD technique. These include the following:

- The definition of an adverse response;
- Selection of response data to model;
- The form of the data used (continuous versus quantal);
- The choice of the measures of increased risk (extra risk versus additional risk);
- The choice of mathematical model (including use of nonstandard models for unusual data sets);
- The selection of the BMR;
- Methods for calculating the confidence interval;
- Selection of the appropriate BMD as the basis for the RfD (when multiple endpoints are modeled from a single study, when multiple models are applied to a single response, and when multiple BMDs are calculated from different studies); and
- The use of uncertainty factors with the BMD approach.

These topics are discussed in detail in Crump et al. (1995) and in the Risk Assessment TSD Volume (USEPA, 2000). The use of the BMD approach has been discussed in general terms by several authors (Gaylor, 1983; Crump, 1984; Dourson et al., 1985; Kimmel and Gaylor, 1988; Brown and Erdreich, 1989; Kimmel, 1990). The International Life Sciences Institute

(ILSI) also held a major workshop on the BMD in September 1993; the workshop proceedings are summarized in ILSI (1993) and in Barnes et al. (1995). For further information on these technical issues, the reader is referred to the publications referenced above.

The BMD approach addresses several of the quantitative or statistical criticisms of the NOAEL approach. These are discussed at greater length in Crump et al. (1995) and are summarized here. First, the BMD approach uses all the dose-response information in the selected study rather than just a single data point, such as the NOAEL or LOAEL. By using response data from all of the dose groups to model a dose-response curve, the BMD approach allows for consideration of the steepness of the slope of the curve when estimating the ED_{10}. The use of the full data set also makes the BMD approach less sensitive to small changes in data than the NOAEL approach, which relies on the statistical comparison of individual dose groups. The BMD approach also allows consistency in the consideration of the level of effect (e.g., a 10 percent response rate) across endpoints.

The BMD approach accounts more appropriately for the size of each dose group than the NOAEL approach. Laboratory tests with fewer animals per dose group tend to yield higher NOAELs, and thus higher RfDs, because statistically significant differences in response rates are harder to detect. Therefore, in the NOAEL approach, dose groups with fewer animals lead to a higher (less conservative) RfD. In contrast, with the BMD approach, smaller dose groups will tend to have the effect of extending the confidence interval around the ED_{10}; therefore, the lower confidence limit on the ED_{10} (the BMD) will be lower. With the BMD approach, greater uncertainty (smaller test groups) leads to a lower (more conservative) RfD.

There are some issues to be resolved before the BMD approach is used routinely. These were identified in a 1996 Peer Consultation Workshop (USEPA, 1996b). Methods for routine use of the BMD are currently under development by EPA. Several RfCs and RfDs based on the BMD approach are included in EPA's IRIS database. These include reference values for methylmercury based on delayed postnatal development in humans; carbon disulfide based on neurotoxicity; 1,1,1,2-tetrafluoroethane based on testicular effects in rats; and antimony trioxide based on chronic pulmonary interstitial inflammation in female rats.

Various mathematical approaches have been proposed for modeling developmental toxicity data (e.g., Crump, 1984; Kimmel and Gaylor, 1988; Rai and Van Ryzin, 1985; Faustman et al., 1989), which could be used to calculate a BMD. Similar methods can be used to model other types of toxicity data, such as neurotoxicity data (Gaylor and Slikker, 1990, 1992; Glowa and MacPhail, 1995). The choice of the mathematical model may not be critical, as long as estimation is within the observed dose range. Since the model fits a mathematical equation to the observed data, the assumptions in a particular model regarding the existence or absence of a threshold for the effect may not be pertinent (USEPA, 1997). Thus, any model that suitably fits the empirical data is likely to provide a reasonable estimate of a BMD. However, research has shown that flexible models that are nonsymmetric (e.g., the Weibull) are superior to symmetric models (e.g., the probit) in estimating the BMD because the data points at the higher doses have less influence on the shape of the curve than at low doses. In addition, models should incorporate fundamental biological factors where such factors are known (e.g., intralitter correlation for developmental toxicity data) in order to account for as much variability in the

data as possible. The Agency is currently using the BMD approach in risk assessments where the data support its use. Draft guidelines for application of the BMD approach also are being developed by the Agency.

Use of BMD methods involves fitting mathematical models to dose-response data obtained primarily from toxicology studies. When considering available models to use for a BMD analysis, it is important to select the model that fits the data the best and is the most biologically appropriate. EPA has developed software following several years of research and development, expert peer review, public comment, subsequent revision, and quality assurance testing. The software (BMDS, Version 1.2) can be downloaded from http://www.epa.gov/ncea/bmds.htm. BMDS facilitates these operations by providing simple data-management tools, a comprehensive help manual, an online help system, and an easy-to-use interface to run multiple models on the same dose-response data.

As part of this software package, EPA has included sixteen (16) different models that are appropriate for the analysis of dichotomous (quantal) data (Gamma, Logistic, Log-Logistic, Multistage, Probit, Log-Probit, Quantal-Linear, Quantal-Quadratic, Weibull), continuous data (Linear, Polynomial, Power, Hill), and nested developmental toxicology data (NLogistic, NCTR, Rai & Van Ryzin). Results from all models include a reiteration of the model formula and model run options chosen by the user, goodness-of-fit information, the BMD, and the estimate of the lower-bound confidence limit on the benchmark dose (BMDL). Model results are presented in textual and graphical output files which can be printed or saved and incorporated into other documents.

B. Categorical Regression

Categorical regression is an emerging technique that may have relevance for the derivation of RfDs or for estimating risk above the RfD (Dourson et al., 1997; Guth et al., 1997). The categorical regression approach, like the BMD approach, can be used to estimate a dose that corresponds to a given probability of adverse effects. This dose would then be divided by UFs to establish an RfD. However, unlike the BMD approach, the Categorical regression approach can incorporate information on different health endpoints in a single dose-response analysis. For those health effects for which studies exist, responses to the substance in question are grouped into severity categories; for example (1) no effect, (2) no adverse effect, (3) mild-to-moderate adverse effect, and (4) frank effect. These categories correspond to the dose categories currently used in setting the RfD, namely, the no-observed-effect level (NOEL), NOAEL, LOAEL, and frank-effect level (FEL), respectively. Logistic transformation or other applicable mathematical operations are used to model the probability of experiencing effects in a certain category as a function of dose (Harrell, 1986; Hertzberg, 1989). The "acceptability" of the fit of the model to the data can be judged using several statistical measures, including the χ^2 statistic, correlation coefficients, and the statistical significance of its model parameter estimates.

The resulting mathematical equation can be used to find a dose (or the lower confidence bound on the dose) at which the probability of experiencing adverse effects does not exceed a selected level, e.g., 10 percent. This dose (like the NOAEL or BMD) would then be divided by

relevant UFs to calculate an RfD. For more detail on how to employ the categorical regression approach, see the discussion in the Risk Assessment TSD (USEPA, 2000).

As with the BMD approach, the categorical regression approach has the advantage of using more of the available dose-response data to account for response variability as well as accounting for uncertainty due to sample size through the use of confidence intervals. Additional advantages of categorical regression include the combining of data sets prior to modeling, thus allowing the calculation of the slope of a dose-response curve for multiple adverse effects rather than only one effect at a time. Another advantage is the ability to estimate risks for different levels of severity from exposures above the RfD.

On the other hand, as with BMD, opinions differ over the amount and adequacy of data necessary to implement the method. The categorical regression approach also requires judgments regarding combining data sets, judging goodness-of-fit, and assigning severity to a particular effect. Furthermore, this approach is still in the developmental stage. It is not recommended for routine use, but may be used when data are available and justify the extensive analyses required.

C. Summary

Whether a NOAEL/UF-based methodology, a BMD, a categorical regression model, or other approach is used to develop the RfD, the dose-response-evaluation step of a risk assessment process should include additional discussion about the nature of the toxicity data and its applicability to human exposure and toxicity. The discussion should present the range of doses that are effective in producing toxicity for a given agent; the route, timing, and duration of exposure; species specificity of effects; and any toxicokinetic or other considerations relevant to extrapolation from the toxicity data to human-health-based AWQC. This information should always accompany the characterization of the adequacy of the data.

3.2.3.2 Presenting the RfD as a Single Point or as a Range for Deriving AWQC

Although the RfD has traditionally been presented and used as a single point, its definition contains the phrase ". . . an estimate (with uncertainty spanning perhaps an order of magnitude) . . ." (USEPA, 1993a). Underlying this concept is the reasoning that the selection of the critical effect and the total uncertainty factor used in the derivation of the RfD is based on the "best" scientific judgment, and that competent scientists examining the same database could derive RfDs which varied within an order of magnitude.

In one instance, IRIS presented the RfD as a point value within an accompanying range. EPA derived a single number as the RfD for arsenic (0.3 μg/kg-day), but added that "strong scientific arguments can be made for various values within a factor of 2 or 3 of the currently recommended RfD value, i.e., 0.1 to 0.8 μg/kg/day" (USEPA, 1993c). EPA noted that regulatory managers should be aware of the flexibility afforded them through this action.

There are situations in which the risk manager can select an alternative value to use in place of the RfD in the AWQC calculations. The domain from which this alternative value can

be selected is restricted to a defined range around the point estimate. As explained further below, the Agency is recommending that sometimes the use of a value other than the calculated RfD point estimate is appropriate in characterizing risk. The selection of an alternative value within an appropriate range must be determined for each individual situation, since several factors affect the selection of the alternative value. Observing similar effects in several animal species, including humans, can increase confidence in the selection of the critical effect and thereby narrow the range of uncertainty. There are other factors that can affect the precision. These include the slope of the dose-response curve, seriousness of the observed effect, dose spacing, and possibly the route for the experimental doses. Dose spacing and the number of animals in the study groups used in the experiment can also affect the confidence in the RfD.

To derive the AWQC, the calculated point estimate of the RfD is the default. Based on consideration of the available data, the use of another number within the range defined by the product of the UF(s) (and MF, if used) could be justified in some specific situations. This means that there are risk considerations which indicate that some value in the range other than the point estimate may be more appropriate, based on human health or environmental fate considerations. For example, the bioavailability of the contaminant in fish tissues is one factor to consider. If bioavailability from fish tissues is much lower than that from water and the RfD was derived from a study in which the contaminant exposure was from drinking water, the alternative to the calculated RfD could be selected from the high end of the range and justified using the quantitative difference in bioavailability.

Most inorganic contaminants, particularly divalent cations, have bioavailability values of 20 percent or less from a food matrix, but are much more available (about 80 percent or higher) from drinking water. Accordingly, the external dose necessary to produce a toxic internal dose would likely be higher for a study where the exposure occurred through the diet rather than the drinking water. As a result, the RfD from a dietary study would likely be higher than that for the drinking water study if equivalent external doses had been used. Conversely, in cases where the NOAEL that was the basis for the RfD came from a dietary study, the alternative value could be slightly lower than the calculated RfD.

Because the uncertainty around the dose-response relationship increases as extrapolation below the observed data increases, the use of an alternative point within the range may be more appropriate in characterizing the risk than the use of the calculated RfD, especially in situations when the uncertainty is high. Therefore, as a matter of policy, the 2000 Human Health Methodology permits the selection of a single point within a range about the calculated RfD to be used as the basis of the AWQC if an adequate justification of the alternative point is provided. More complete discussion of this option, including limitations on the span of the range, is provided in the Risk Assessment TSD (USEPA, 2000).

3.2.3.3 Guidelines to be Adopted for Derivation of Noncancer Health Effects Values

The Agency currently is using the IRIS background document as the general basis for the risk assessment of noncarcinogenic effects of chemicals (USEPA, 1993a). EPA recommends continued use of this document for this purpose. However, it should be noted that the process for evaluating chemicals for inclusion in IRIS is undergoing revision (USEPA, 1996c). The

revised assessments for many chemicals are now available on IRIS and can be consulted as examples of the RfD development process and required supporting documentation.

3.2.3.4 Treatment of Uncertainty Factors/Severity of Effects During the RfD Derivation and Verification Process

During the RfD derivation and toxicology review process, EPA considers the uncertainty in extrapolating between animal species and within individuals of a species, as well as specific uncertainties associated with the completeness of the database. The Agency's RfD Work Group has always considered the severity of the observed effects induced by the chemical under review when choosing the value of the UF with a LOAEL. For example, during the derivation and verification of the RfD for zinc (USEPA, 1992), an uncertainty factor less than the standard factor of 10 (UF of 3) was assigned to the relatively mild decrease in erythrocyte superoxide dismutase activity in human subjects. EPA recommends that the severity of the critical effect be assessed when deriving an RfD and that risk managers be made aware of the severity of the effect and the weight placed on this attribute of the effect when the RfD was derived.

3.2.3.5 Use of Less-Than-90-Day Studies to Derive RfDs

Generally, less-than-90-day experimental studies are not used to derive an RfD. This is based on the rationale that studies lasting for less than 90 days may be too short to detect various toxic effects. However, EPA, has in certain circumstances, derived an RfD based on a less-than-90-day study. For example, the RfD for nonradioactive effects of uranium is based on a 30-day rabbit study (USEPA, 1989). The short-term exposure period was used, because it was adequate for determining doses that cause chronic toxicity. In other cases, it may be appropriate to use a less-than-90-day study because the critical effect is expressed in less than 90 days. For example, the RfD for nitrate was derived and verified using studies that were less than 3-months in duration (USEPA, 1991b). For nitrate, the critical effect of methemoglobinemia in infants occurs in less than 90 days. When it can be demonstrated from other data in the toxicological database that the critical adverse effect is expressed within the study period and that a longer exposure duration would not exacerbate the observed effect or cause the appearance of some other adverse effect, the Agency may choose to use less-than-90-day studies as the basis of the RfD. Such values would have to be used with care because of the uncertainty in determining if other effects might be expressed if exposure was of greater duration than 90 days.

3.2.3.6 Use of Reproductive/Developmental, Immunotoxicity, and Neurotoxicity Data as the Basis for Deriving RfDs

All relevant toxicity data have some bearing on the RfD derivation and verification and are considered by EPA. The "critical" effect is the adverse effect most relevant to humans or, in the absence of an effect known to be relevant to humans, the adverse effect that occurs at the lowest dose in animal studies. If the critical effect is neurotoxicity, EPA will use that endpoint as the basis for the derivation and verification of an RfD, as it did for the RfD for acrylamide. Moreover, the Agency is continually revising its procedures for noncancer risk assessment. For example, EPA has released guidelines for deriving developmental RfDs (RfD_{DT}, USEPA, 1991a), for using reproductive toxicity (USEPA, 1996a), and neurotoxicity (USEPA, 1995) data

in risk assessments. The Agency is currently working on guidelines for using immunotoxicity data to derive RfDs. In addition, the Agency is proceeding with the process of generating acceptable emergency health levels for hazardous substances in acute exposure situations based on established guidelines (NRC, 1993).

3.2.3.7 Applicability of Toxicokinetic Data in Risk Assessment

All pertinent toxicity data should be used in the risk assessment process, including toxicokinetic and mechanistic data. The Agency has used toxicokinetic data in deriving the RfD for cadmium and other compounds and currently is using toxicokinetic data to better characterize human inhalation exposures from animal inhalation experiments during derivation/verification of RfCs. In analogy to the RfD, the RfC is considered to be an estimate of a concentration in the air that is not anticipated to cause adverse noncancer effects over a lifetime of inhalation exposure (USEPA, 1994; Jarabek, 1995a). For RfCs, different dosimetry adjustments are made to account for the differences between laboratory animals and humans in gas uptake and disposition or in particle clearance and retention. This procedure results in calculation of a "human equivalent concentration." Based on the use of these procedures, an interspecies UF of 3 (i.e., approximately $10^{0.5}$), instead of the standard factor of 10, is used in the RfC derivation (Jarabek, 1995b).

Toxicokinetics and toxicodynamics of a chemical each contribute to a chemical's observed toxicity, and specifically, to observed differences among species in sensitivity. Toxicokinetics describes the disposition (i.e., deposition, absorption, distribution, metabolism, and elimination of chemicals in the body) and can be approximated using toxicokinetic models. Toxicodynamics describes the toxic interaction of the agent with the target cell. In the absence of specific data on their relative contributions to the toxic effects observed in species, each is considered to account for approximately one-half of the difference in observed effects for humans compared with laboratory animals. The implication of this assumption is that an interspecies uncertainty factor of 3 rather than 10 could be used for deriving an RfD when valid toxicokinetic data and models can be applied to obtain an oral "human equivalent applied dose" (Jarabek, 1995b). If specific data exist on the relative contribution of either element to observed effects, that proportion will be used. The role exposure duration may play, and whether or not the chemical or its damage may accumulate over time in a particular scenario, also requires careful consideration (Jarabek, 1995c).

3.2.3.8 Consideration of Linearity (or Lack of a Threshold) for Noncarcinogenic Chemicals

It is quite possible that there are chemicals with noncarcinogenic endpoints that have no threshold for effects. For example, in the case of lead, it has not been possible to identify a threshold for effects on neurological development. Other examples could include genotoxic teratogens and germline mutagens. Genotoxic teratogens act by causing mutational events during organogenesis, histogenesis, or other stages of development. Germline mutagens interact with germ cells to produce mutations which may be transmitted to the zygote and expressed during one or more stages of development. However, there are few chemicals which currently have sufficient mechanistic information about these possible modes of action. It should be recognized that although an MOA consistent with linearity is possible (especially for agents

known to be mutagenic), this has yet to be reasonably demonstrated for most toxic endpoints other than cancer.

EPA has recognized the potential for nonthreshold noncarcinogenic endpoints and discussed this issue in the *Guidelines for Developmental Toxicity Risk Assessment* (USEPA, 1991a) and in the 1986 *Guidelines for Mutagenicity Risk Assessment* (USEPA, 1986). An awareness of the potential for such teratogenic/mutagenic effects should be established in order to deal with such data. However, without adequate data to support a genetic or mutational basis for developmental or reproductive effects, the default becomes a UF or MOA approach, which are procedures utilized for noncarcinogens assumed to have a threshold. Therefore, genotoxic teratogens and germline mutagens should be considered an exception while the traditional uncertainty factor approach is the general rule for calculating criteria or values for chemicals demonstrating developmental/reproductive effects. For the exceptional cases, since there is no well-established mechanism for calculating criteria protective of human health from the effects of these agents, criteria will be established on a case-by-case basis. Other types of nonthreshold noncarcinogens must also be handled on a case-by-case basis.

3.2.3.9 Minimum Data Guidance

For details on minimum data guidance for RfD development, see the Risk Assessment TSD (USEPA, 2000).

3.2.4 References for Noncancer Effects

Allen, B.C., R.T. Kavlock, C.A. Kimmel, and E.M. Faustman. 1994. Dose-response assessment for developmental toxicity. *Fund. Appl. Toxicol*. 23:496-509.

Barnes, D.G., G.P Daston, J.S. Evans, A.M. Jarabek, R.J. Kavlock, C.A. Kimmel, C. Park, and H.L. Spitzer. 1995. Benchmark dose workshop: criteria for use of a benchmark dose to estimate a reference dose. *Reg. Toxicol. Pharmacol*. 21:296-306.

Brown, K.G. and L.S. Erdreich. 1989. Statistical uncertainty in the no-observed-adverse-effect level. *Fund. Appl. Toxicol.* 13:235-244.

Crump, K.S., B. Allen, and E. Faustman. 1995. *The Use of the Benchmark Dose Approach in Health Risk Assessment*. Prepared for U.S. Environmental Protection Agency's Risk Assessment Forum. EPA/630/R-94/007.

Crump, K.S. 1984. A new method for determining acceptable daily intakes. *Fund. Appl. Toxicol*. 4:854-871.

Dourson, M.L. 1994. Methodology for establishing oral reference doses (RfDs). In: *Risk Assessment of Essential Elements.* W. Mertz, C.O. Abernathy, and S.S. Olin (eds.) ILSI Press. Washington, DC. Pp. 51-61.

Dourson, M.L., R.C. Hertzberg, R. Hartung and K. Blackburn. 1985. Novel approaches for the estimation of acceptable daily intake. *Toxicol. Ind. Health* 1:23-41.

Dourson, M.L., L.K. Teuschler, P.R. Durkin, and W.M. Stiteler. 1997. Categorical regression of toxicity data, a case study using aldicarb. *Regul. Toxicol. Pharmacol*. 25:121-129.

Faustman, E.M., D.G. Wellington, W.P. Smith and C.A. Kimmel. 1989. Characterization of a developmental toxicity dose-response model. *Environ. Health Perspect.* 79:229-241.

Gaylor, D.W. 1983. The use of safety factors for controlling risk. *J. Toxicol. Environ. Health* 11:329-336.

Gaylor, D.W. and W. Slikker. 1990. Risk assessment for neurotoxic effects. Neurotoxicology 11:211-218.

Gaylor, D.W. and W. Slikker. 1992. Risk assessment for neurotoxicants. In: *Neurotoxicology.* H. Tilson and C. Mitchel (eds). Raven Press. New York, NY. Pp. 331-343.

Glowa, J.R. and R.C. MacPhail. 1995. Quantitative approaches to risk assessment in neurotoxicology. In: *Neurotoxicology: Approaches and Methods.* Academic Press. New York, NY. Pp. 777-787.

Guth, D.J., R.J. Carroll, D.G. Simpson, and H. Zhou. 1997. Categorical regression analysis of acute exposure to tetrachloroethylene. *Risk Anal.* 17(3):321-332.

Harrell, F. 1986. The logist procedure. *SUGI Supplemental Library Users Guide*, Ver. 5th ed. SAS Institute. Cary, NC.

Hertzberg, R.C. 1989. Fitting a model to categorical response data with application to species extrapolation of toxicity. *Health Physics* 57: 405-409.

ILSI (International Life Sciences Institute). 1993. *Report of the Benchmark Dose Workshop*. ISLI Risk Science Institute. Washington, DC.

Jarabek, A.M. 1995a. The application of dosimetry models to identify key processes and parameters for default dose-response assessment approaches. *Toxicol. Lett.* 79:171-184.

Jarabek, A.M. 1995b. Interspecies extrapolation based on mechanistic determinants of chemical disposition. *Human Eco. Risk Asses*. 1(5):41-622.

Jarabek, A.M. 1995c. Consideration of temporal toxicity challenges current default assumptions. Inhalation Toxicol. 7:927-946.

Kimmel, C.A. 1990. Quantitative approaches to human risk assessment for noncancer health effects. *Neurotoxicology* 11: 189-198.

Kimmel, C.A. and D.W. Gaylor. 1988. Issues in qualitative and quantitative risk analysis for developmental toxicity. *Risk Anal*. 8: 15-20.

NRC (National Research Council). 1977. *Decision Making in the Environmental Protection Agency. Vol. 2.* National Academy of Sciences. Washington, DC. Pp. 32-33 and 241-242.

NRC (National Research Council). 1993. *Guidelines for Developing Emergency Exposure Levels for Hazardous Substances*. Subcommittee on Guidelines for Developing Community Emergency Exposure Levels (CEELs) for Hazardous Substances. Committee on Toxicology, NRC. National Academy Press. Washington, DC.

Rai, K. and J. Van Ryzin. 1985. A dose-response model for teratological experiments involving quantal responses. *Biometrics* 41: 1-10.

USEPA (U.S. Environmental Protection Agency). 1986. Guidelines for mutagenicity assessment. *Federal Register* 51:34006-34012. September 24.

USEPA (U.S. Environmental Protection Agency). 1989. Reference dose (RfD) for oral exposure for uranium (soluble salts). *Integrated Risk Information System (IRIS). Online*. (Verification date 10/1/89). Office of Health and Environmental Assessment, Environmental Criteria and Assessment Office. Cincinnati, OH.

USEPA (U.S. Environmental Protection Agency). 1991a. Final guidelines for developmental toxicity risk assessment. *Federal Register* 56:63798-63826. December 5.

USEPA (U.S. Environmental Protection Agency). 1991b. Reference dose (RfD) for oral exposure for nitrate. *Integrated Risk Information System (IRIS). Online*. (Verification date 10/01/91). Office of Health and Environmental Assessment, Environmental Criteria and Assessment Office. Cincinnati, OH.

USEPA (U.S. Environmental Protection Agency). 1992. Reference dose (RfD) for oral exposure for inorganic zinc. *Integrated Risk Information System (IRIS). Online*. (Verification date 10/1/92). Office of Health and Environmental Assessment, Environmental Criteria and Assessment Office. Cincinnati, OH.

USEPA (U.S. Environmental Protection Agency). 1993a. Reference dose (RfD): Description and use in health risk assessments. *Integrated Risk Information System (IRIS). Online.* Intra-Agency Reference Dose (RfD) Work Group, Office of Health and Environmental Assessment, Environmental Criteria and Assessment Office. Cincinnati, OH. March 15.

USEPA (U.S. Environmental Protection Agency). 1993b. *Revision of Methodology for Deriving National Ambient Water Quality Criteria for the Protection of Human Health: Report of Workshop and EPA's Preliminary Recommendations for Revision*. Submitted to the EPA Science Advisory Board by the Human Health Risk Assessment Branch, Health and Ecological Criteria Division, Office of Science and Technology, Office of Water. Washington, DC. January 8.

USEPA (U.S. Environmental Protection Agency). 1993c. Reference dose (RfD) for oral exposure for inorganic arsenic. *Integrated Risk Information System (IRIS). Online.* (Verification date 02/01/93). Office of Health and Environmental Assessment, Environmental Criteria and Assessment Office. Cincinnati, OH.

USEPA (U.S. Environmental Protection Agency). 1994. *Methods for Derivation of Inhalation Reference Concentrations and Application of Inhalation Dosimetry*. Office of Health and Environmental Assessment, Environmental Criteria and Assessment Office. Research Triangle Park, NC. EPA/600/8-90/066F.

USEPA (U.S. Environmental Protection Agency). 1995. Proposed guidelines for neurotoxicity risk assessment. *Federal Register* 60:52032-52056. October 4.

USEPA (U.S. Environmental Protection Agency). 1996a. Reproductive toxicity risk assessment guidelines. *Federal Register* 61:56274-56322. October 31.

USEPA (U.S. Environmental Protection Agency). 1996b. *Report on the Benchmark Dose Peer Consultation Workshop.* Risk Assessment Forum. Washington, DC. EPA/630/R-96/011.

USEPA (U.S. Environmental Protection Agency). 1996c. Integrated Risk Information System (IRIS); announcement of pilot program; request for information. *Federal Register*. 61: 14570. April 2.

USEPA (U.S. Environmental Protection Agency). 1997. *Mercury Study: Report to Congress. Volume 5: Health Effects of Mercury and Mercury Compounds.* Office of Air Quality Planning and Standards, and Office of Research and Development. Research Triangle Park, NC. EPA-452-R-97-007.

USEPA (U.S. Environmental Protection Agency). 2000. *Methodology for Deriving Ambient Water Quality Criteria for the Protection of Human Health (2000). Technical Support Document Volume 1: Risk Assessment.* Office of Science and Technology, Office of Water. Washington, DC. EPA-822-B-00-005. August.

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4. EXPOSURE

The derivation of AWQC for the protection of human health requires information about both the toxicological endpoints of concern for water pollutants and the pathways of human exposure to those pollutants. The two primary pathways of human exposure to pollutants present in a particular ambient waterbody that have been considered in deriving AWQC are direct ingestion of drinking water obtained from that waterbody and the consumption of fish/shellfish obtained from that waterbody. The water pathway also includes other exposures from household uses (e.g., showering). The derivation of an AWQC involves the calculation of the maximum water concentration for a pollutant (i.e., the water quality criteria level) that ensures drinking water and/or fish ingestion exposures will not result in human intake of that pollutant in amounts that exceed a specified level based upon the toxicological endpoint of concern.

The equation for noncancer effects is presented again here, in simplified form, to emphasize the exposure-related parameters (in bold). [Note: the RSC parameter also applies to nonlinear low-dose extrapolation for cancer effects and the other exposure parameters apply to all three of the equations (see Section 1.6).]

$$AWQC = RfD \bullet \boldsymbol{RSC} \bullet \frac{(\boldsymbol{BW})}{\left[\boldsymbol{DI} + (\boldsymbol{FI} \bullet BAF)\right]} \qquad \text{(Equation 4-1)}$$

where:

AWQC	=	Ambient Water Quality Criterion (mg/L)
RfD	=	Reference dose for noncancer effects (mg/kg-day)
RSC	=	Relative source contribution factor to account for non-water sources of exposure
BW	=	Human body weight (kg)
DI	=	Drinking water intake (L/day)
FI	=	Fish intake (kg/day)
BAF	=	Bioaccumulation factor (L/kg)

The following subsections discuss exposure issues relevant to the 2000 Human Health Methodology: exposure policy issues; consideration of non-water sources of exposure (the Relative Source Contribution approach); and the factors used in AWQC computation. In relevant sections, science policy and risk management decisions made by EPA are discussed.

4.1 EXPOSURE POLICY ISSUES

This section discusses broad policy issues related to exposure concerning the major objectives that the Agency believes should be met in setting AWQC.

An Exposure Assessment TSD provides greater detail on numerous topics discussed in this guidance: suggested sources of contaminant concentration and exposure intake information; suggestions of survey methods for obtaining and analyzing exposure data necessary for deriving AWQC; summaries of studies on fish consumption among sport fishers and subsistence fishers; more detailed presentation of parameter values (e.g., fish consumption rates, body weights); and additional guidance on the application of the RSC approach.

4.1.1 Sources of Exposure Associated With Ambient Water

4.1.1.1 Appropriateness of Including the Drinking Water Pathway in AWQC

EPA intends to continue including the drinking water exposure pathway in the derivation of its national default human health criteria (AWQC), as has been done since the 1980 AWQC National Guidelines were first published.

EPA recommends inclusion of the drinking water exposure pathway where drinking water is a designated use for the following reasons: (1) Drinking water is a designated use for surface waters under the CWA and, therefore, criteria are needed to assure that this designated use can be protected and maintained. (2) Although rare, there are some public water supplies that provide drinking water from surface water sources without treatment. (3) Even among the majority of water supplies that do treat surface waters, existing treatments may not necessarily be effective for reducing levels of particular contaminants. (4) In consideration of the Agency's goals of pollution prevention, ambient waters should not be contaminated to a level where the burden of achieving health objectives is shifted away from those responsible for pollutant discharges and placed on downstream users to bear the costs of upgraded or supplemental water treatment.

This policy decision has been supported by the States, most of the public stakeholders, and by external peer reviewers. As with the other exposure parameters, States and authorized Tribes have the flexibility to use alternative intake rates if they believe that drinking water consumption is substantively different than EPA's recommended default assumptions of 2 L/day for adults and 1 L/day for children. EPA recommends that States and authorized Tribes use an intake rate that would be protective of a majority of consumers and will consider whether an alternative assumption is adequately protective of a State's or Tribe's population based on the information or rationale provided at the time EPA reviews State and Tribal water quality standards submissions.

4.1.1.2 Setting Separate AWQC for Drinking Water and Fish Consumption

In conjunction with the issue of the appropriateness of including the drinking water pathway explicitly in the derivation of AWQC for the protection of human health, EPA intends to continue its practice of setting a single AWQC for both drinking water and fish/shellfish consumption, and a separate AWQC based on ingestion of fish/shellfish alone. This latter criterion applies in those cases where the designated uses of a waterbody include supporting fishable uses under Section 101(a) of the CWA and, thus, fish or shellfish for human consumption, but not as a drinking water supply source (e.g., non-potable estuarine waters).

EPA does not believe that national water quality criteria for protection of drinking water uses only are particularly useful for two reasons. First, State and Tribal standards for human health are set to protect Section 101(a) uses (e.g., "fishable, swimmable uses") under the CWA. Second, most waters have multiple designated uses. Additionally, the water quality standards program protects aquatic life. The 2000 Human Health Methodology revisions do not change EPA's policy to apply aquatic life criteria to protect aquatic species where they are more sensitive (i.e., when human health criteria would not be protective enough) or where human health via fish or water ingestion is not an issue.

4.1.1.3 Incidental Ingestion from Ambient Surface Waters

The 2000 Human Health Methodology does not routinely include criteria to address incidental ingestion of water from recreational uses. EPA has considered whether there are cases where water quality criteria for the protection of human health based only on fish ingestion (or only criteria for the protection of aquatic life) may not adequately protect recreational users from health effects resulting from incidental water ingestion.

EPA reviewed information that provided estimates of incidental water ingestion rates averaged over time. EPA generally believes that the averaged amount is negligible and will not have any impact on the chemical criteria values representative of both drinking water and fish ingestion. A lack of impact on the criteria values would likely also be true for chemical criteria based on fish consumption only, unless the chemical exhibits no bioaccumulation potential. However, EPA also believes that incidental/accidental water ingestion could be important for the development of microbial contaminant water quality criteria, and for either chemical or microbial criteria for States where recreational uses such as swimming and boating are substantially higher than the national average. EPA also notes that some States have indicated they already have established incidental ingestion rates for use in developing criteria. Therefore, although EPA will not use this intake parameter when deriving its national 304(a) chemical criteria, limited guidance is provided in the Exposure Assessment TSD volume in order to assist States and authorized Tribes that face situations where this intake parameter could be of significance.

4.2 CONSIDERATION OF NON-WATER SOURCES OF EXPOSURE WHEN SETTING AWQC

4.2.1 Policy Background

The 2000 Human Health Methodology uses different approaches for addressing non-water exposure pathways in setting AWQC for the protection of human health depending upon the toxicological endpoint of concern. With those substances for which the appropriate toxic endpoint is carcinogenicity based on a linear low-dose extrapolation, only the two water sources (i.e., drinking water and fish ingestion) are considered in the derivation of the AWQC. Non-water sources are not considered explicitly. In the case of carcinogens based on linear low-dose extrapolation, the AWQC is being determined with respect to the *incremental* lifetime risk posed by a substance's presence in water, and is not being set with regard to an individual's total risk from all sources of exposure. Thus, the AWQC represents the water concentration that would be

expected to increase an individual's lifetime risk of carcinogenicity from exposure to the particular pollutant by no more than one chance in one million, regardless of the additional lifetime cancer risk due to exposure, if any, to that particular substance from other sources.

Furthermore, health-based criteria values for one medium based on linear low-dose extrapolation typically vary from values for other media in terms of the concentration value, and often the associated risk level. Therefore, the RSC concept could not even theoretically apply unless all risk assessments for a particular carcinogen based on linear low-dose extrapolation resulted in the same concentration value and same risk level; that is, an apportionment would need to be based on a single risk value and level.

In the case of substances for which the AWQC is set on the basis of a carcinogen based on a nonlinear low-dose extrapolation or for a noncancer endpoint where a threshold is assumed to exist, non-water exposures are considered when deriving the AWQC using the RSC approach. The rationale for this approach is that for pollutants exhibiting threshold effects, the objective of the AWQC is to ensure that an individual's total exposure does not exceed that threshold level.

There has been some discussion of whether it is, in fact, necessary in most cases to explicitly account for other sources of exposure when computing the AWQC for pollutants exhibiting threshold effects. It has been argued that because of the conservative assumptions generally incorporated in the calculation of RfDs (or POD/UF values) used as the basis for the AWQC derivation, total exposures slightly exceeding the RfD are unlikely to produce adverse effects.

EPA emphasizes that the purpose of the RSC is to ensure that the level of a chemical allowed by a criterion or multiple criteria, when combined with other identified sources of exposure common to the population of concern, will not result in exposures that exceed the RfD or the POD/UF. The policy of considering multiple sources of exposure when deriving health-based criteria has become common in EPA's program office risk characterizations and criteria and standard-setting actions. Numerous EPA workgroups have evaluated the appropriateness of factoring in such exposures, and the Agency concludes that it is important for adequately protecting human health. Consequently, EPA risk management policy has evolved significantly over the last six years. Various EPA program initiatives and policy documents regarding aggregate exposure and cumulative risk have been developed, including the consideration of inhalation and dermal exposures. Additionally, accounting for other exposures has been included in recent mandates (e.g., the Food Quality Protection Act) and, thus, is becoming a requirement for the Agency. The Exposure Decision Tree approach has been shared with other EPA offices, and efforts to coordinate policies on aggregate exposure, where appropriate, have begun. EPA intends to continue developing policy guidance on the RSC issue and guidance to address the concern that human health may not be adequately protected if criteria allow for higher levels of exposure that, combined, may exceed the RfD or POD/UF. EPA also intends to refine the 2000 Human Health Methodology in the future to incorporate additional guidance on inhalation and dermal exposures. As stated previously, EPA is required to derive national water quality criteria under Section 304(a) of the CWA and does not intend to derive site-specific criteria. However, States and authorized Tribes have the flexibility to make alternative exposure and RSC estimates based on local data, and EPA strongly encourages this.

Uncertainty factors used in the derivation of the RfD (or POD/UF) to account for intra- and interspecies variability and the incompleteness of the toxicity data set(s)/animal studies are specifically relevant to the chemical's internal toxicological action, irrespective of the sources of exposure that humans may be experiencing. The Agency's policy is to consider and account for other sources of exposure in order to set protective health criteria. EPA believes that multiple route exposures may be particularly important when uncertainty factors associated with the RfD are small. Although EPA is well aware that RfDs are not all equivalent in their derivation, EPA does not believe that uncertainty in the toxicological data should result in less stringent criteria by ignoring exposure sources. However, the RSC policy approach does allow less stringent assumptions when multiple sources of exposure are not anticipated.

The AWQC are designed to be protective criteria, generally applicable to the waters of the United States. While EPA cannot quantitatively predict the actual human health risk associated with combined exposures above the RfD or POD/UF, a combination of health criteria for multiple media exceeding the RfD or POD/UF may not be sufficiently protective. Therefore, EPA's policy is to routinely account for all sources and routes of non-occupational exposure when setting AWQC for noncarcinogens and for carcinogens based on nonlinear low-dose extrapolations. EPA believes that maintaining total exposure below the RfD (or POD/UF) is a reasonable health goal and that there are circumstances where health-based criteria for a chemical should not exceed the RfD (or POD/UF), either alone (if only one criterion is relevant, along with other intake sources considered as background exposures) or in combination. EPA believes its RSC policy ensures this goal.

Also, given the inability to reasonably predict future changes in exposure patterns, the uncertainties in the exposure estimates due to typical data inadequacy, possible unknown sources of exposure, and the potential for some populations to experience greater exposures than indicated by the available data, EPA believes that utilizing the entire RfD (or POD/UF) does not ensure adequate protection.

4.2.2 The Exposure Decision Tree Approach

As indicated in Section 1, EPA has, in the past, used a "subtraction" method to account for multiple sources of exposure to pollutants. In the subtraction method, other sources of exposure (i.e., those other than the drinking water and fish exposures) are subtracted from the RfD (or POD/UF). However, EPA also previously used a "percentage" method for the same purpose. In this approach, the percentage of total exposure typically accounted for by the exposure source for which the criterion is being determined, referred to as the relative source contribution (RSC), is applied to the RfD to determine the maximum amount of the RfD "apportioned" to that source. With both procedures, a "ceiling" level of 80 percent of the RfD and a "floor level" of 20 percent of the RfD are applied.

The subtraction method is considered acceptable when only one criterion is relevant for a particular chemical. The percentage method is recommended in the context of the above goals when multiple media criteria are at issue. The percentage method does not simply depend on the amount of a contaminant in the prospective criterion source only. It is intended to reflect health considerations, the relative portions of other sources, and the likelihood for ever-changing levels

in each of those multiple sources (due to ever-changing sources of emissions and discharges). Rather than simply defaulting in every instance, the Agency attempts to compare multiple source exposures with one another to estimate their relative contribution to the total–given that understanding the degree to which their concentrations vary, or making any distributional analysis, is often not possible. The criteria levels, when multiple criteria are at issue, are based on the actual levels, with an assumption that there may be enough relative variability such that an apportionment (relating that percentage to the RfD) is a reasonable way of accounting for the uncertainty regarding that variability.

The specific RSC approach recommended by EPA, which we will use for the derivation of AWQC for noncarcinogens and carcinogens assessed using nonlinear low-dose extrapolation, is called the Exposure Decision Tree and is described below. To account for exposures from other media when setting an AWQC (i.e., non-drinking water/non-fish ingestion exposures, and inhalation or dermal exposures), the Exposure Decision Tree for determining proposed RfD or POD/UF apportionments represents a method of comprehensively assessing a chemical for water quality criteria development. This method considers the adequacy of available exposure data, levels of exposure, relevant sources/media of exposure, and regulatory agendas (i.e., whether there are multiple health-based criteria or regulatory standards for the same chemical). The Decision Tree addresses most of the disadvantages associated with the exclusive use of either the percentage or subtraction approaches, because they are not arbitrarily chosen prior to determining the following: specific population(s) of concern, whether these populations are relevant to multiple-source exposures for the chemical in question (i.e., whether the population is actually or potentially experiencing exposure from multiple sources), and whether levels of exposure, regulatory agendas, or other circumstances make apportionment of the RfD or POD/UF desirable. Both subtraction and percentage methods are potentially utilized under different circumstances with the Exposure Decision Tree approach, and the Decision Tree is recommended with the idea that there is enough flexibility to use other procedures if information on the contaminant in question suggests it is not appropriate to follow the Decision Tree. EPA recognizes that there may be other valid approaches in addition to the Exposure Decision Tree.

The Exposure Decision Tree approach allows flexibility in the RfD (or POD/UF) apportionment among sources of exposure. When adequate data are available, they are used to make protective exposure estimates for the population(s) of concern. When other sources or routes of exposure are anticipated but data are not adequate, there is an even greater need to make sure that public health protection is achieved. For these circumstances, a series of qualitative alternatives is used (with the less adequate data or default assumptions) that allow for the inadequacies of the data while protecting human health. Specifically, the Decision Tree makes use of chemical information when actual monitoring data are inadequate. It considers information on the chemical/physical properties, uses of the chemical, and environmental fate and transformation, as well as the likelihood of occurrence in various media. Review of such information, when available, and determination of a reasonable exposure characterization for the chemical will result in a water quality criterion that more accurately reflects exposures than automatically using a default value. Although the 20 percent default will still generally be used when information is not adequate, the need for using it should be reduced. There may also be some situations where EPA would consider the use of an 80 percent default (see Section 4.2.3).

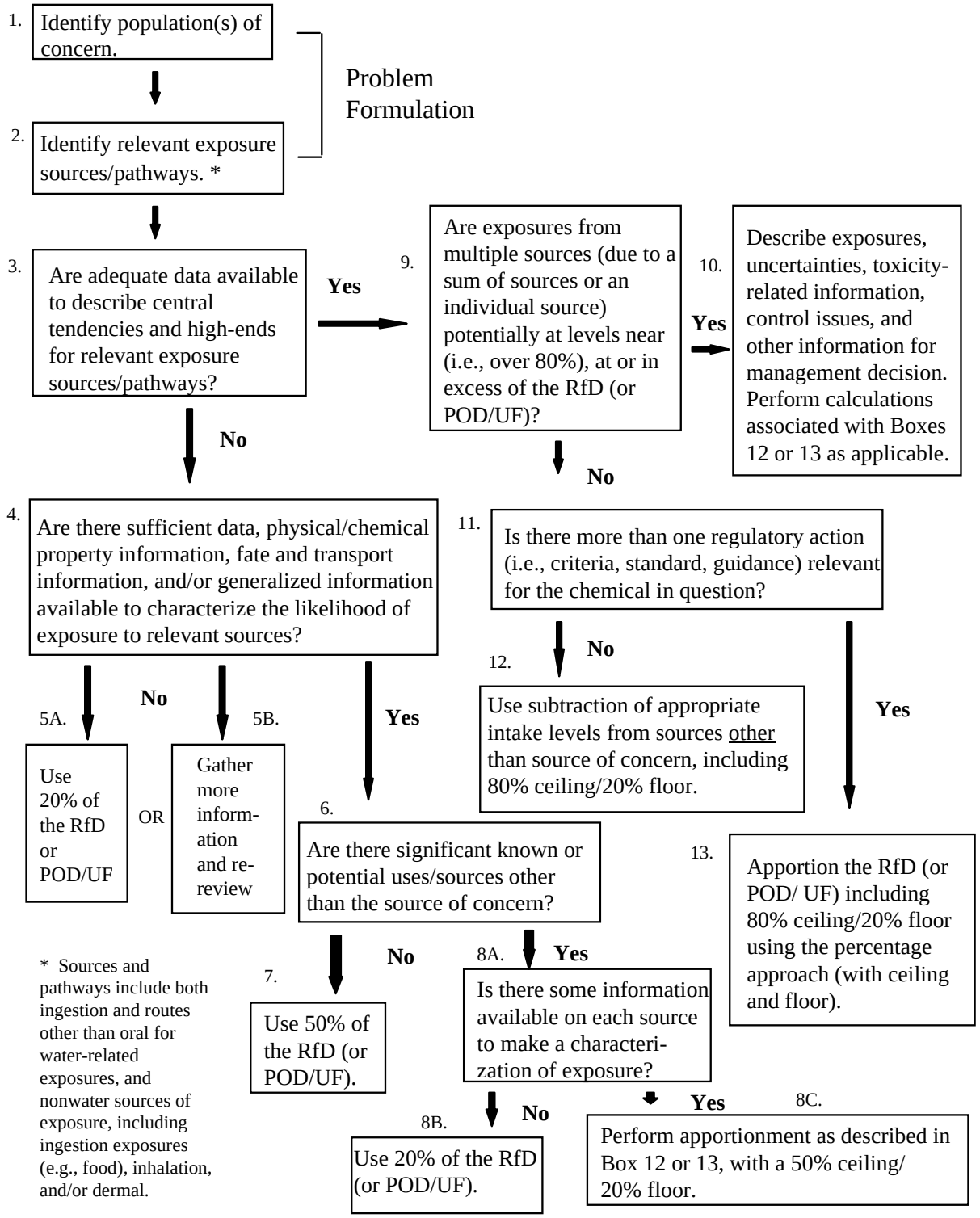
The Decision Tree also allows for use of either the subtraction or percentage method to account for other exposures, depending on whether one or more health-based criterion is relevant for the chemical in question. The subtraction method is considered acceptable when only one criterion is relevant for a particular chemical. In these cases, other sources of exposure can be considered "background" and can be subtracted from the RfD (or POD/UF).

EPA cautions States and Tribes when using the subtraction method in these circumstances. The subtraction method results in a criterion allowing the maximum possible chemical concentration in water after subtracting other sources. As such, it removes any cushion between pre-criteria levels (i.e., actual "current" levels) and the RfD, thereby setting criteria at the highest levels short of exceeding the RfD. It is somewhat counter to the goals of the CWA for maintaining and restoring the nation's waters. It is also directly counter to Agency policies, explicitly stated in numerous programs, regarding pollution prevention. EPA has advocated that it is good health policy to set criteria such that exposures are kept low when current levels are already low. The subtraction method generally results in criteria levels of a contaminant in a particular medium at significantly higher levels than the percentage method and, in this respect, is contradictory to such goals. In fact, many chemicals have pre-criteria levels in environmental media substantially lower (compared to the RfD) than the resulting criteria allow.

When more than one criterion is relevant to a particular chemical, apportioning the RfD (or POD/UF) via the percentage method is considered appropriate to ensure that the combination of criteria and, thus, the potential for resulting exposures do not exceed the RfD (or POD/UF). The Exposure Decision Tree (with numbered boxes) is shown in Figure 4-1. The explanation in the text on the following pages must be read in tandem with the Decision Tree figure; the text in each box of the figure only nominally identifies the process and conditions for determining the outcome for that step of the Decision Tree. The underlying objective is to maintain total exposure below the RfD (or POD/UF) while generally avoiding an extremely low limit in a single medium that represents just a nominal fraction of the total exposure. To meet this objective, all proposed numeric limits lie between 80 percent and 20 percent of the RfD (or POD/UF). Again, EPA will use the Exposure Decision Tree approach when deriving its AWQC but also recognizes that departures from the approach may be appropriate in certain cases. EPA understands that there may be situations where the Decision Tree procedure is not practicable or

Figure 4-1

Exposure Decision Tree for Defining Proposed RfD (or POD/UF) Apportionment



may be simply irrelevant after considering the properties, uses, and sources of the chemical in question. EPA endorses such flexibility by States and authorized Tribes when developing alternative water quality criteria in order to choose other procedures that are more appropriate for setting health-based criteria and, perhaps, apportioning the RfD or POD/UF, as long as reasons are given as to why it is not appropriate to follow the Exposure Decision Tree approach and as long as the steps taken to evaluate the potential sources and levels of exposure are clearly described. Often, however, the common situation of multiple exposure sources for a chemical is likely to merit a Decision Tree evaluation for the purpose of developing human health water quality criteria for a given chemical.

It is clear that this will be an interactive process; input by exposure assessors will be provided to, and received from, risk managers throughout the process, given that there may be significant implications regarding control issues (i.e., cost/feasibility), environmental justice issues, etc. In cases where the Decision Tree is not chosen, communication and concurrence about the decision rationale and the alternative water quality criteria are of great importance.

Descriptions of the boxes within the Decision Tree are separated by the following process headings to facilitate an understanding of the major considerations involved. The decision to perform, or not to perform, an apportionment could actually be made at several points during the Decision Tree process. Working through the process is most helpful for identifying possible exposure sources and the potential for exposure, determining the relevancy of the Decision Tree to developing an AWQC for a particular chemical and, possibly, determining the appropriateness of using an alternative approach to account for overall exposure. "Relevancy" here means determining whether more than one criterion, standard, or other guidance is being planned or is in existence for the chemical in question. Additional guidance for States and Tribes that wish to use the Exposure Decision Tree is provided in the Exposure Assessment TSD.

4.2.2.1 Problem Formulation

Initial Decision Tree discussion centers around the first two boxes: identification of population(s) of concern (Box 1) and identification of relevant exposure sources and pathways (Box 2). The term "problem formulation" refers to evaluating the population(s) and sources of exposure in a manner that allows determination of the potential for the population of concern to experience exposures from multiple sources for the chemical in question. Also, the data for the chemical in question must be representative of each source/medium of exposure and be relevant to the identified population(s). Evaluation includes determining whether the levels, multiple criteria or regulatory standards, or other circumstances make apportionment of the RfD or POD/UF reasonable. The initial problem formulation also determines the exposure parameters chosen, the intake assumptions chosen for each route, and any environmental justice or other social issues that aid in determining the population of concern. The term "data," as used here and discussed throughout this section, refers to ambient sampling data (whether from Federal, regional, State, or area-specific studies) and not internal human exposure measurements.

4.2.2.2 Data Adequacy

In Box 3, it is necessary that adequate data exist for the relevant sources/pathways of exposure if one is to avoid using default procedures. The adequacy of data is a professional judgment for each individual chemical of concern, but EPA recommends that the minimum acceptable data for Box 3 are exposure distributions that can be used to determine, with an acceptable 95 percent confidence interval, the central tendency and high-end exposure levels for each source. In fact, distributional data may exist for some or most of the sources of exposure.

There are numerous factors to consider in order to determine whether a dataset is adequate. These include: (1) sample size (i.e., the number of data points); (2) whether the data set is a random sample representative of the target population (if not, estimates drawn from it may be biased no matter how large the sample); (3) the magnitude of the error that can be tolerated in the estimate (estimator precision); (4) the sample size needed to achieve a given precision for a given parameter (e.g., a larger sample is needed to precisely estimate an upper percentile than a mean or median value); (5) an acceptable analytical method detection limit; and (6) the functional form and variability of the underlying distribution, which determines the estimator precision (e.g., whether the distribution is normal or lognormal and whether the standard deviation is 1 or 10). Lack of information may prevent assessment of each of these factors; monitoring study reports often fail to include background information or sufficient summary statistics (and rarely the raw data) to completely characterize data adequacy. Thus, a case-by-case determination of data adequacy may be necessary.

That being stated, there are some guidelines, as presented below, that lead to a rough rule-of-thumb on what constitutes an "adequate" sample size for exposure assessment. Again, first and foremost, the representativeness of the data for the population evaluated and the analytical quality of the data must be acceptable. If so, the primary objective then becomes estimating an upper percentile (e.g., say the 90th) and a central tendency value of some exposure distribution based on a random sample from the distribution. Assuming that the distribution of exposures is unknown, a nonparametric estimate of the 90th percentile is required. The required estimate, based on a random sample of *n* observations from a target population, is obtained by ranking the data from smallest to largest and selecting the observation whose rank is 1 greater than the largest integer in the product of 0.9 times *n*. For example, in a data set of 25 points, the nonparametric estimate of the 90th percentile is the 23rd largest observation.

In addition to this point estimate, it is useful to have an upper confidence bound on the 90th percentile. To find the rank of the order statistic that gives an upper 95 percent confidence limit on the 90th percentile, the smallest value of *r* that satisfies the following formula is determined:

$$0.95 \approx \sum_{i=0}^{r-1} \binom{n}{i} 0.9^{i}\ 0.1^{n-i} \qquad \text{(Equation 4-2)}$$

where:

r	=	the rank order of the observation
n	=	the number of observations
I	=	integer from 0 to r - 1

For relatively small data sets, the above formula will lead to selecting the largest observation as the upper confidence limit on the 90th percentile. However, the problem with using the maximum is that, in many environmental datasets, the largest observation is an outlier and would provide an unrealistic upper bound on the 90th percentile. It would, therefore, be preferable if the sample size *n* were large enough so that the formula yielded the second largest observation as the confidence limit (see for example Gibbons, 1971).

This motivates establishing the following criterion for setting an "adequate" sample size: pick the smallest *n* such that the nonparametric upper 95 percent confidence limit on the 90th percentile is the second largest value. Application of the above formula with *r* set to *n*-1 yields *n* = 45 for this minimum sample size.

For the upper 95 percent confidence limit to be a useful indicator of a high-end exposure, it must not be overly conservative (too large relative to the 90th percentile). It is, therefore, of interest to estimate the expected magnitude of the ratio of the upper 95 percent confidence limit to the 90th percentile. This quantity generally cannot be computed, since it is a function of the unknown distribution. However, to get a rough idea of its value, consider the particular case of a normal distribution. If the coefficient of variation (i.e., the standard deviation divided by the mean) is between 0.5 and 2.0, the expected value of the ratio in samples of 45 will be approximately 1.17 to 1.31; i.e., the upper 95 percent confidence limit will be only about 17 to 31 percent greater than the 90th percentile on the average.

It should be noted that the nonparametric estimate of the 95 percent upper confidence limit based on the second largest value can be obtained even if the data set has only two detects (it is assumed that the two detects are greater than the detection limit associated with all non-detects). This is an argument for using nonparametric rather than parametric estimation, since use of parametric methods would require more detected values. On the other hand, if non-detects were not a problem and the underlying distribution were known, a parametric estimate of the 90th percentile would generally be more precise.

As stated above, adequacy also depends on whether the samples are relevant to and representative of the population at risk. Data may, therefore, be adequate for some decisions and inadequate for others; this determination requires some professional judgment.

If the answer to Box 3 is no, based on the above determination of adequacy, then the decision tree moves to Box 4. As suggested by the separate boxes, the available data that will be reviewed as part of Box 4 do not meet the requirements necessary for Box 3. In Box 4, any limited data that are available (in addition to information about the chemical/physical properties, uses, and environmental fate and transformation, as well as any other information that would characterize the likelihood of exposure from various media for the chemical) are evaluated to

make a qualitative determination of the relation of one exposure source to another. Although this information should always be reviewed at the outset, it is recommended that this information also be used to estimate the health-based water quality criteria. The estimate should be rather conservative (as indicated in the Decision Tree), given that it is either not based on actual monitoring data or is based on data that has been considered to be inadequate for a more accurate quantitative estimate. Therefore, greater uncertainties exist and accounting for variability is not really possible. Whether the available data are adequate and sufficiently representative will likely vary from chemical to chemical and may depend on the population of concern. If there are some data and/or other information to make a characterization of exposure, a determination can be made as to whether there are significant known or potential uses for the chemical/sources of exposure other than the source of concern (i.e., in this case, the drinking water and fish intakes relevant to developing an AWQC) that would allow one to anticipate/quantify those exposures (Box 6). If there are not, then it is recommended that 50 percent of the RfD or POD/UF can be safely apportioned to the source of concern (Box 7). While this leaves half of the RfD or POD/UF unapportioned, it is recommended as the maximum apportionment due to the lack of data needed to more accurately quantify actual or potential exposures. If the answer to the question in Box 6 is yes (there is multiple source information available for the exposures of concern), and some information is available on each source of exposure (Box 8A), apply the procedure in either Box 12 or Box 13 (depending on whether one or more criterion is relevant to the chemical), using a 50 percent ceiling (Box 8C)–again due to the lack of adequate data. If the answer to the question in Box 8A is no (there is no available information to characterize exposure), then the 20 percent default of the RfD or POD/UF is used (Box 8B).

If the answer to the question in Box 4 is no; that is, there are not sufficient data/information to characterize exposure, EPA intends to generally use the "default" assumption of 20 percent of the RfD or POD/UF (Box 5A) when deriving or revising the AWQC. It may be better to gather more data or information and re-review when this information becomes available (Box 5B). EPA has done this on occasion when resources permit the acquisition of additional data to enable better estimates of exposure instead of the default. If this is not possible, then the assumption of 20 percent of the RfD or POD/UF (Box 5A) should be used. Box 5A is likely to be used infrequently with the Exposure Decision Tree approach, given that the information described in Box 4 should be available in most cases. However, EPA intends to use 20 percent of the RfD (or POD/UF), which has also been used in past water program regulations, as the default value.

4.2.2.3 Regulatory Actions

If there are adequate data available to describe the central tendencies and high ends from each exposure source/pathway, then the levels of exposure relative to the RfD or POD/UF are compared (Box 9). If the levels of exposure for the chemical in question are not near (currently defined as greater than 80 percent), at, or in excess of the RfD or POD/UF, then a subsequent determination is made (Box 11) as to whether there is more than one health-based criterion or regulatory action relevant for the given chemical (i.e., more than one medium-specific criterion,

standard or other guidance being planned, performed or in existence for the chemical). The subtraction method is considered acceptable when only one criterion (standard, etc.) is relevant for a particular chemical. In these cases, other sources of exposure can be considered "background" and can be subtracted from the RfD (or POD/UF). When more than one criterion is relevant to a particular chemical, apportioning the RfD (or POD/UF) via the percentage method is considered appropriate to ensure that the combination of health criteria, and thus the potential for resulting exposures, do not exceed the RfD (or POD/UF).

As indicated in Section 2, for EPA's national 304(a) criteria, the RSC intake estimates of non-water exposures (e.g., non-fish dietary exposures) will be based on arithmetic mean values when data are available. The assumed body weight used in calculating the national criteria will also be based on average values. The drinking water and fish intake values are 90th percentile estimates. EPA believes that these assumptions will be protective of a majority of the population and recommends them for State and Tribal use. However, States and authorized Tribes have the flexibility to choose alternative intake rate and exposure estimate assumptions to protect specific population groups that they have chosen.

4.2.2.4 Apportionment Decisions

If the answer to the question in Box 11 is no (there is not more than one relevant medium-specific criterion/regulatory action), then the recommended method for setting a health-based water quality criterion is to utilize a subtraction calculation (Box 12). Specifically, appropriate intake values for each exposure source other than the source of concern are subtracted out. EPA will rely on average values commonly used in the Agency for food ingestion and inhalation rates, combined with mean contaminant concentration values, for calculating RSC estimates to subtract. Alternatively, contaminant concentrations could be selected based on the variability associated with those concentrations for each source. This implies that a case-by-case determination of the variability and the resulting intake chosen would be made, as each chemical evaluated can be expected to have different variations in concentration associated with each source of intake. However, EPA anticipates that the available data for most contaminants will not allow this for determination (based on past experience). Guidance addressing this possibility is addressed in the Exposure Assessment TSD. EPA does not recommend that high-end intakes be subtracted for every exposure source, since the combination may not be representative of any actually exposed population or individual. The subtraction method would also include an 80 percent ceiling and a 20 percent floor.

If the answer to the question in Box 11 is yes (there is more than one medium-specific criterion/regulation relevant), then the recommended method for setting health-based water quality criteria is to apportion the RfD or POD/UF among those sources for which health-based criteria are being set (Box 13). This is done via a percentage approach (with a ceiling and floor). This simply refers to the percentage of overall exposure contributed by an individual exposure source. For example, if for a particular chemical, drinking water were to represent half of total exposure and diet were to represent the other half, then the drinking water contribution (or RSC) would be 50 percent. The health-based criteria would, in turn, be set at 50 percent of the RfD or POD/UF. This method also utilizes an appropriate combination of intake values for each

exposure source based on values commonly used in the Agency for food ingestion and inhalation rates, combined with mean contaminant concentration values.

Finally, if the levels of exposure for the chemical in question are near (currently defined as greater than 80 percent), at, or in excess of the RfD or POD/UF (i.e., the answer in Box 9 is yes), then the estimates of exposures and related uncertainties, recommended apportionment (either box 12 or 13), toxicity-related information, control issues, and other information are to be presented to managers for a decision (Box 10). The high levels referred to in Box 9 may be due to one source contributing that high level (while other sources contribute relatively little) or due to more than one source contributing levels that, in combination, approach or exceed the RfD or POD/UF. Management input may be necessary due to the control issues (i.e., cost and feasibility concerns), especially when multiple criteria are at issue. In practice, risk managers are routinely a part of decisions regarding regulatory actions and will be involved with any recommended outcome of the Exposure Decision Tree or, for that matter, any alternative to the Exposure Decision Tree. However, because exposures approach or exceed the RfD or POD/UF and because the feasibility of controlling different sources of exposure are complicated issues, risk managers will especially need to be directly involved in final decisions in these circumstances.

It is emphasized here that the procedures in these circumstances are not different than the procedures when exposures are not at or above the RfD (or POD/UF). Therefore, in these cases, estimates should be performed as with Boxes 11, 12, and 13. The recommendation should be made based on health-based considerations only, just as when the chemical in question was not a Box 10 situation. If the chemical is relevant to one health criterion or regulatory action only, the other sources of exposure could be subtracted from the RfD or POD/UF to determine if there is any leftover amount for setting the criterion. If the chemical is a multiple media criteria issue, then an apportionment should be made, even though it is possible that all sources would need to be reduced. Regardless of the outcome of Box 9, all apportionments made (via the methods of Boxes 12 or 13) should include a presentation of the uncertainty in the estimate and in the RfD or POD/UF for a more complete characterization.

The process for a Box 10 situation (versus a situation that is not) differs in that the presentations for Boxes 12 and 13 are based on apportionments (following the review of available information and a determination of appropriate exposure parameters) that must address additional control issues and may result in more selective reductions. With Box 10, one or several criteria possibilities ("scenarios") could be presented for comparison along with implications of the effects of various control options. It is appropriate to present information in this manner to risk managers given the complexity of these additional control issues.

4.2.3 Additional Points of Clarification on the Exposure Decision Tree Approach for Setting AWQC

As with Box 9, if a determination is made in Box 8A (i.e., information is available to characterize exposure) that exposures are near, at, or above the RfD (or POD/UF) based on the available information, the apportionments made need to be presented to risk managers for decision. If information is lacking on some of the multiple exposure sources, then EPA would use a default of 20 percent of the RfD or POD/UF (Box 8B).

Results of both Boxes 12 and 13 rely on the 80 percent ceiling and 20 percent floor. The 80 percent ceiling was implemented to ensure that the health-based goal will be low enough to provide adequate protection for individuals whose total exposure to a contaminant is, due to any of the exposure sources, higher than currently indicated by the available data. This also increases the margin of safety to account for possible unknown sources of exposure. The 20 percent floor has been traditionally rationalized to prevent a situation where small fractional exposures are being controlled. That is, below that point, it is more appropriate to reduce other sources of exposure, rather than promulgating standards for *de minimus* reductions in overall exposure.

If it can be demonstrated that other sources and routes of exposure are not anticipated for the pollutant in question (based on information about its known/anticipated uses and chemical/physical properties), then EPA would use the 80 percent ceiling. EPA qualifies this policy with the understanding that as its policy on cumulative risk assessment continues to develop, the 80 percent RSC may prove to be underprotective.

In the cases of pollutants for which substantial data sets describing exposures across all anticipated pathways of exposure exist, and probabilistic analyses have been conducted based on those data, consideration will be given to the results of those assessments as part of the Exposure Decision Tree approach for setting AWQC.

For many chemicals, the rate of absorption from ingestion can differ substantially from absorption by inhalation. There is also available information for some chemicals that demonstrates appreciable differences in gastrointestinal absorption depending on whether the chemical is ingested from water, soil, or food. For some contaminants, the absorption of the contaminant from food can differ appreciably for plant compared with animal food products. Regardless of the apportionment approach used, EPA recommends using existing data on differences in bioavailability between water, air, soils, and different foods when estimating total exposure for use in apportioning the RfD or POD/UF. The Agency has developed such exposure estimates for cadmium (USEPA, 1994). In the absence of data, EPA will assume equal rates of absorption from different routes and sources of exposure.

4.2.4 Quantification of Exposure

When selecting contaminant concentration values in environmental media and exposure intake values for the RSC analysis, it is important to realize that each value selected (including those recommended as default assumptions in the AWQC equation) may be associated with a distribution of values for that parameter. Determining how various subgroups fall within the distributions of overall exposure and how the combination of exposure variables defines what population is being protected is a complicated and, perhaps, unmanageable task, depending on the amount of information available on each exposure factor included. Many times, the default assumptions used in EPA risk assessments are derived from the evaluation of numerous studies and are considered to generally represent a particular population group or a national average. Therefore, describing with certainty the exact percentile of a particular population that is protected with a resulting criteria is often not possible.

By and large, the AWQC are derived to protect the majority of the general population from chronic adverse health effects. However, as stated above in Section 4.1.1.1, States and authorized Tribes are encouraged to consider protecting population groups that they determine are at greater risk and, thus, would be better protected using alternative exposure assumptions. The ultimate choice of the contaminant concentrations used in the RSC estimate and the exposure intake rates requires the use of professional judgment. This is discussed in greater detail in the Exposure Assessment TSD.

4.2.5 Inclusion of Inhalation and Dermal Exposures

EPA intends to develop policy guidelines to apply to this Methodology for explicitly incorporating inhalation and dermal exposures. When estimating overall exposure to pollutants for AWQC development, EPA believes that the sources of inhalation and dermal exposures considered should include, on a case-by-case basis, both non-oral exposures from water and other inhalation and dermal sources (e.g., ambient or indoor air, soil). When the policy guidelines are completed, this Methodology will be refined to include that guidance.

A number of drinking water contaminants are volatile and thus diffuse from water into the air where they may be inhaled. In addition, drinking water is used for bathing and, thus, there is at least the possibility that some contaminants in water may be dermally absorbed. Volatilization may increase exposure via inhalation and decrease exposure via ingestion and dermal absorption. The net effect of volatilization and dermal absorption upon total exposure to volatile drinking water contaminants is unclear in some cases and varies from chemical to chemical. Dermal exposures are also important to consider for certain population groups, such as children and other groups with high soil contact.

With regard to additional non-water related exposures, it is clear that the type and magnitude of toxicity produced via inhalation, ingestion, and dermal contact may differ; that is, the route of exposure can affect absorption of a chemical and can otherwise modify its toxicity. For example, an inhaled chemical such as hydrogen fluoride may produce localized effects on the lung that are not observed (or only observed at much higher doses) when the chemical is administered orally. Also, the active form of a chemical (and principal toxicity) can be the parent compound and/or one or more metabolites. With this Methodology, EPA recommends that differences in absorption and toxicity by different routes of exposure be determined and accounted for in dose estimates and applied to the exposure assessment. EPA acknowledges that the issue of whether the doses received from inhalation and ingestion exposures are cumulative (i.e., toward the same threshold of toxicity) is complicated. Such a determination involves evaluating the chemical's physical characteristics, speciation, and reactivity. A chemical may also exhibit different metabolism by inhalation versus oral exposure and may not typically be metabolized by all tissues. In addition, a metabolite may be much more or much less toxic than the parent compound. Certainly with a systemic effect, if the chemical absorbed via different routes enters the bloodstream, then there is some likelihood that it will contact the same target organ. Attention also needs to be given to the fact that both the RfD and RfC are derived based on the administered level. Toxicologists generally believe that the effective concentration of the active form of a chemical(s) at the site(s) of action determines the toxicity. If specific differences between routes of exposure are not known, it may be reasonable to assume that the

internal concentration at the site from any route contributes as much to the same effect as any other route. A default of assuming equal absorption has often been used. However, for many of the chemicals that the Agency has reviewed, there is a substantial amount of information already known to determine differences in rates of absorption. For example, absorption is, in part, a function of blood solubility (i.e., Henry's Constant) and better estimations than the default can be made.

The RSC analyses that accompany the 2000 Human Health Methodology accommodate inclusion of inhalation exposures. Even if different target organs are involved between different routes of exposure, a conservative policy may be appropriate to keep all exposures below a certain level. A possible alternative is to set allowable levels (via an equation) such that the total of ingestion exposures over the ingestion RfD added to the total of inhalation exposures over the inhalation RfC is not greater than 1 (Note: the RfD is typically presented in mg/kg-day and the RfC is in mg/m^3). Again, EPA intends to develop guidance for this Methodology to explicitly incorporate inhalation and dermal exposures, and will refine the Methodology when that guidance is completed.

4.3 EXPOSURE FACTORS USED IN THE AWQC COMPUTATION

This section presents values for the specific exposure factors that EPA will use in the derivation of AWQC. These include human body weight, drinking water consumption rates, and fish ingestion rates.

When choosing exposure factor values to include in the derivation of a criterion for a given pollutant, EPA recommends considering values that are relevant to population(s) that is (are) most susceptible to that pollutant. In addition, highly exposed populations should be considered when setting criteria. In general, exposure factor values specific to adults and relevant to lifetime exposures are the most appropriate values to consider when determining criteria to protect against effects from long-term exposure which, by and large, the human health criteria are derived to protect. However, infants and children may have higher rates of water and food consumption per unit body weight compared with adults and also may be more susceptible to some pollutants than adults (USEPA, 1997a). There may be instances where acute or subchronic developmental toxicity makes children the population group of concern. In addition, exposure of pregnant women to certain toxic chemicals may cause developmental effects in the fetus (USEPA, 1997b). Exposures resulting in developmental effects may be of concern for some contaminants and should be considered along with information applicable to long-term health effects when setting AWQC. (See Section 3.2 for further discussion of this issue.) Short-term exposure may include multiple intermittent or continuous exposures occurring over a week or so. Exposure factor values relevant for considering chronic toxicity, as well as exposure factor values relevant for short-term exposure developmental concerns, that could result in adverse health effects are discussed in the sections below. In appropriate situations, EPA may consider developing criteria for developmental health effects based on exposure factor values specific to children or to women of childbearing age. EPA encourages States and Tribes to do the same when health risks are associated with short-term exposures.

EPA believes that the recommended exposure factor default intakes for adults in chronic exposure situations are adequately protective of the population over a lifetime. In providing additional exposure intake values for highly exposed subpopulations (e.g., sport anglers, subsistence fishers), EPA is providing flexibility for States and authorized Tribes to establish criteria specifically targeted to provide additional protection using adjusted values for exposure parameters for body weight, drinking water intake, and fish consumption. The exposure factor values provided for women of childbearing age and children would only be used in the circumstances indicated above.

Each of the following sections recommends exposure parameter values for use in developing AWQC. These are based on both science policy decisions that consider the best available data, as well as risk management judgments regarding the overall protection afforded by the choice in the derivation of AWQC. These will be used by EPA to derive new, or revise existing, 304(a) national criteria.

4.3.1 Human Body Weight Values for Dose Calculations

The source of data for default human body weights used in deriving the AWQC is the third *National Health and Nutrition Examination Survey* (NHANES III). NHANES III represents a very large interview and examination endeavor of the National Center for Health Statistics (NCHS) and included participation from the Centers for Disease Control (CDC). The NHANES III was conducted on a nationwide probability sample of over 30,000 persons from the civilian, non-institutionalized population of the United States. The survey began in October 1988 and was completed in October 1994 (WESTAT, 2000; McDowell, 2000). Body weight data were taken from the NHANES III Examination Data File. Sampling weights were applied to all persons examined in the Mobile Examination Centers (MECs) or at home, as was recommended by the NHANES data analysts (WESTAT, 2000).

The NHANES III survey has numerous strengths and very few weaknesses. Its primary strengths are the national representativeness, large sample size, and precise estimates due to this large sample size. Another strength is its high response rate; the examination rate was 73 percent overall, 89 percent for children under 1 year old, and approximately 85 percent for children 1 to 5 years old (McDowell, 2000). Interview response rates were even higher, but the body weight data come from the NHANES examinations; that is, all body weights were carefully measured by survey staff, rather than the use of self-reported body weights. The only significant potential weakness of the NHANES data is the fact that the data are now between 6 and 12 years old. Given that there were upward trends in body weight from NHANES II to NHANES III, and that NCHS has indicated the prevalence of overweight people increased in all age groups, the data could underestimate current body weights if that trend has continued (WESTAT, 2000).

The NHANES III collected standard body measurements of sample subjects, including height and weight, that were made at various times of the day and in different seasons of the year. This technique was used because one's weight may vary between winter and summer and may fluctuate with recency of food and water intake and other daily activities (McDowell, 2000).

As with the other exposure assumptions, States and authorized Tribes are encouraged to use alternative body weight assumptions for population groups other than the general population and to use local or regional data over default values as more representative of their target population group(s).

4.3.1.1 Rate Protective of Human Health from Chronic Exposure

EPA recommends maintaining the default body weight of 70 kg for calculating AWQC as a representative average value for both male and female adults. As previously indicated, exposure factor values specific to adults are recommended to protect against effects from long-term exposure. The value of 70 kg is based on the following information. In the analysis of the NHANES III database, median and mean values for female adults 18-74 years old are 65.8 and 69.5 kg, respectively (WESTAT, 2000). For males in the same age range, the median and mean values are 79.9 and 82.1 kg, respectively. The mean body weight value for men and women ages 18 to 74 years old from this survey is 75.6 kg (WESTAT, 2000). This mean value is higher than the mean value for adults ages 20-64 years old of 70.5 kg from a study by the National Cancer Institute (NCI) which primarily measured drinking water intake (Ershow and Cantor, 1989). The NCI study is described in the subsection on Drinking Water Intake Rates that follows (Section 4.3.2). The value from the NHANES III database is also higher than the value given in the revised EPA *Exposure Factors Handbook* (USEPA, 1997b), which recommends 71.8 kg for adults, based on the older NHANES II data. The Handbook also acknowledges the commonly used 70 kg value and encourages risk assessors to use values which most accurately reflect the exposed population. However, the point is also made that the 70 kg value is used in the derivation of cancer slope factors and unit risks that appear in IRIS. Consistency is advocated between the dose-response relationship and exposure factors assumed. Therefore, if a value higher than 70 kg is used, the assessor needs to adjust the dose-response relationship as described in the Appendix to Chapter 1, Volume 1 of the Handbook (USEPA, 1997b).

4.3.1.2 Rates Protective of Developmental Human Health Effects

As noted above, pregnant women may represent a more appropriate population for which to assess risks from exposure to chemicals in ambient waters in some cases, because of the potential for developmental effects in fetuses. In these cases, body weights representative of women of childbearing age may be appropriate to adequately protect offspring from such health effects. To determine a mean body weight value appropriate to this population, separate body weight values for women in individual age groups within the range of 15 to 44 years old were analyzed from the NHANES III data (WESTAT, 2000). The resulting median and mean body weight values are 63.2 and 67.3 kg, respectively. Ershow and Cantor (1989) present body weight values specifically for pregnant women included in the survey; median and mean weights are 64.4 and 65.8 kilograms, respectively. Ershow and Cantor (1989), however, do not indicate the ages of these pregnant women. Based on this information for women of childbearing age and pregnant women, EPA recommends use of a body weight value of 67 kg in cases where pregnant women are the specific population of concern and the chemical of concern exhibits reproductive and/or developmental effects (i.e., the critical effect upon which the RfD or POD/UF is based). Using the 67 kg assumption would result in lower (more protective) criteria than criteria based on 70 kg.

As discussed earlier, because infants and children generally have a higher rate of water and food consumption per unit body weight compared with adults, a higher intake rate per unit body weight may be needed when comparing estimated exposure doses with critical doses when RfDs are based on health effects in children. To calculate intake rates relevant to such effects, the body weight of children should be used. As with the default body weight for pregnant women, EPA is not recommending the development of additional AWQC (i.e., similar to drinking water health advisories) that focus on acute or short-term effects, since these are not seen routinely as having a meaningful role in the water quality criteria program. However, there may be circumstances where the consideration of exposures for these groups is warranted. Although the AWQC generally are based on chronic health effects data, they are intended to also be protective with respect to adverse effects that may reasonably be expected to occur as a result of elevated shorter-term exposures. EPA acknowledges this as a potential course of action and is, therefore, recommending these default values which EPA would consider in an appropriate circumstance and for States and authorized Tribes to utilize in such situations.

EPA is recommending an assumption of 30 kg as a default child's body weight to calculate AWQC to provide additional protection for children when the chemical of concern indicates health effects in children are of predominant concern (i.e., test results show children are more susceptible due to less developed immune systems, neurological systems, and/or lower body weights). The value is based on the mean body weight value of 29.9 kg for children ages 1 to14 years old, which combines body weight values for individual age groups within this larger group. The mean value is based on body weight information from NHANES III for individual-year age groups between one and 14 years old (WESTAT, 2000). A mean body weight of 28 kg is obtained using body weight values from Ershow and Cantor (1989) for five age groups within this range of 0-14 years and applying a weighting method for different ages by population percentages from the U.S. Bureau of the Census. The 30 kg assumption is also consistent with the age range for children used with the estimated fish intake rates. Unfortunately, fish intake rates for finer age group divisions are not possible due to the limited sampling base from the fish intake survey; there is limited confidence in calculated values (e.g., the mean) for such fine age groups. Given this limitation, the broad age category of body weight for children is suitable for use with the default fish intake assumption.

Given the hierarchy of preferences regarding the use of fish intake information (see Section 4.3.3), States may have more comprehensive data and prefer to target a more narrow, younger age group. If States choose to specifically evaluate toddlers, EPA recommends using 13 kg as a default body weight assumption for children ages 1 to 3 years old. The median and mean values of body weight for children 1 to 3 years old are 13.2 and 13.1 kg, respectively, based on an analysis of the NHANES III database (WESTAT, 2000). The NHANES III median and mean values for females between 1 and 3 years old are 13.0 and 12.9 kg, respectively, and are 13.4 and 13.4 kg for males, respectively. Median and mean body weight values from the earlier Ershow and Cantor (1989) study for children ages 1 to 3 years old were 13.6 and 14.1 kg, respectively. Finally, if infants are specifically evaluated, EPA recommends a default body weight of 7 kg based on the NHANES III analysis. Median and mean body weights for both male and female infants (combined) 2 months old were 6.3 and 6.3 kg, respectively, and for infants 3 months old were 7.0 and 6.9 kg, respectively. With the broader age category of males and females 2 to 6 months old, median and mean body weights were 7.4 and 7.4 kg, respectively. The NHANES

analysis did not include infants under 2 months of age. Although EPA is not recommending body weight values for newborns, the NCHS National Vital Statistics Report indicates that, for 1997, the median birth weight ranged from 3 to 3.5 kg, according to WESTAT (2000).

Body weight values for individual ages within the larger range of 0-14 years are listed in the Exposure Assessment TSD for those States and authorized Tribes who wish to use body weight values for these individual groups. States and Tribes may wish to consider certain general developmental ages (e.g., infants, pre-adolescents, etc.), or certain specific developmental landmarks (e.g., neurological development in the first four years), depending on the chemical of concern. EPA encourages States and authorized Tribes to choose a body weight intake from the tables presented in the TSD, if they believe a particular age subgroup is more appropriate.

4.3.2 Drinking Water Intake Rates

The basis for the drinking water intake rates (also for the fish intake rates presented in Section 4.3.3) is the 1994-96 Continuing Survey of Food Intake by Individuals *(*CSFII) conducted by the U.S. Department of Agriculture (USDA, 1998). The CSFII survey collects dietary intake information from nationally representative samples of non-institutionalized persons residing in United States households. Households in these national surveys are sampled from the 50 states and the District of Columbia. Each survey collects daily consumption records for approximately 10,000 food codes across nine food groups. These food groups are (1) milk and milk products; (2) meat, poultry, and fish; (3) eggs; (4) dry beans, peas, legumes, nuts, and seeds; (5) grain products; (6) fruit; (7) vegetables; (8) fats, oils, and salad dressings; and (9) sweets, sugars, and beverages. The survey also asks each respondent how many fluid ounces of plain drinking water he or she drank during each of the survey days. In addition, the CSFII collects household information, including the source of plain drinking water, water used to prepare beverages, and water used to prepare foods. Data provide "up-to-date information on food intakes by Americans for use in policy formation, regulation, program planning and evaluation, education, and research." The survey is "the cornerstone of the National Nutritional Monitoring and Related Research Program, a set of related federal activities intended to provide regular information on the nutritional status of the United States population" (USDA, 1998).

The 1994-96 CSFII was conducted according to a stratified, multi-area probability sample organized using estimates of the 1990 United States population. Stratification accounted for geographic location, degree of urbanization, and socioeconomics. Each year of the survey consisted of one sample with oversampling for low-income households.

Survey participants provided two non-consecutive, 24-hour days of dietary data. Both days' dietary recall information was collected by an in-home interviewer. Interviewers provided participants with an instructional booklet and standard measuring cups and spoons to assist them in adequately describing the type and amount of food ingested. If the respondent referred to a cup or bowl in their own home, a 2-cup measuring cup was provided to aid in the calculation of the amount consumed. The sample person could fill their own bowl or cup with water to represent the amount eaten or drunk, and the interviewer could then measure the amount consumed by pouring it into the 2-cup measure. The Day 2 interview occurred three to 10 days

after the Day 1 interview, but not on the same day of the week. The interviews allowed participants "three passes" through the daily intake record to maximize recall (USDA, 1998). Proxy interviews were conducted for children aged six and younger and sampled individuals unable to report due to mental or physical limitations. The average questionnaire administration time for Day 1 intake was 30 minutes, while Day 2 averaged 27 minutes.

Two days of dietary recall data were provided by 15,303 individuals across the three survey years. This constitutes an overall two-day response rate of 75.9 percent. Survey weights were corrected by the USDA for nonresponse.

All three 1994-96 CSFII surveys are multistage, stratified-cluster samples. Sample weights, which project the data from a sampled individual to the population, are based on the probability of an individual being sampled at each stage of the sampling design. The sample weights associated with each individual reporting two days of consumption data were adjusted to correct for nonresponse bias.

The 1994-96 CSFII surveys have advantages and limitations for estimating per capita water (or fish) consumption. The primary advantage of the CSFII surveys is that they were designed and conducted by the USDA to support unbiased estimation of food consumption across the population in the United States and the District of Columbia. Second, the survey is designed to record daily intakes of foods and nutrients and support estimation of food consumption.

One limitation of the 1994-96 CSFII surveys is that individual food consumption data were collected for only two days–a brief period which does not necessarily depict "usual intake." Usual dietary intake is defined as "the long-run average of daily intakes by an individual." Upper percentile estimates may differ for short-term and longer-term data because short-term food consumption data tend to be inherently more variable. It is important to note, however, that variability due to duration of the survey does not result in bias of estimates of overall mean consumption levels. Also, the multistage survey design does not support interval estimates for many of the subpopulations of interest because of sparse representation in the sample. Subpopulations with sparse representation include Native Americans on reservations and certain ethnic groups. While these individuals are participants in the survey, they are not present in sufficient numbers to support consumption estimates.

Despite these limitations, the CSFII is considered one of the best sources of current information on consumption of water and fish-containing foods. The objective of estimating per capita water and fish consumption by the United States population is compatible with the statistical design and scope of the CSFII survey.

4.3.2.1 Rate Protective of Human Health from Chronic Exposure

EPA recommends maintaining the default drinking water intake rate of 2 L/day to protect most consumers from contaminants in drinking water. EPA believes that the 2 L/day assumption is representative of a majority of the population over the course of a lifetime. EPA also notes that there is comparatively little variability in water intake within the population compared with

fish intake (i.e., drinking water intake varies, by and large, by about a three-fold range, whereas fish intake can vary by 100-fold). EPA believes that the 2 L/day assumption continues to represent an appropriate risk management decision. The results of the 1994-96 CSFII analysis indicate that the arithmetic mean, 75th, and 90th percentile values for adults 20 years and older are 1.1, 1.5, and 2.2 L/day, respectively (USEPA, 2000a). The 2 L/day value represents the 86th percentile for adults. These values can also be compared to data from an older National Cancer Institute (NCI) study, which estimated intakes of tapwater in the United States based on the USDA's 1977-78 Nationwide Food Consumption Survey (NFCS). The arithmetic mean, 75th, and 90th percentile values for adults 20 - 64 years old were 1.4, 1.7, and 2.3 L/day, respectively (Ershow and Cantor, 1989). The 2 L/day value represents the 88th percentile for adults from the NCI study.

The 2 L/day assumption was used with the original 1980 AWQC National Guidelines and has also been used in EPA's drinking water program. EPA believes that the newer studies continue to support the use of 2 L/day as a reasonable and protective consumption rate that represents the intake of most water consumers in the general population. However, individuals who work or exercise in hot climates could have water consumption rates significantly above 2 L/day, and EPA believes that States and Tribes should consider regional or occupational variations in water consumption.

4.3.2.2 Rates Protective of Developmental Human Health Effects

Based on the 1994-96 CSFII study data, EPA also recommends 2 L/day for women of childbearing age. The analysis for women of childbearing age (ages 15-44) indicate mean, 75th, and 90th percentile values of 0.9, 1.3, and 2.0 L/day, respectively. These rates compare well with those based on an analysis of tapwater intake by pregnant and lactating women by Ershow et al. (1991), based on the older USDA data, for women ages 15-49. Arithmetic mean, 75th and 90th percentile values were 1.2, 1.5, and 2.2 L/day, respectively, for pregnant women. For lactating women, the arithmetic mean, 75th and 90th percentile values were 1.3, 1.7, and 1.9 L/day, respectively.

As noted above, because infants and children have a higher daily water intake per unit body weight compared with adults, a water consumption rate measured for children is recommended for use when RfDs are based on health effects in children. Use of this water consumption rate should result in adequate protection for infants and children when setting criteria based on health effects for this target population. EPA recommends a drinking water intake of 1 L/day to, again, represent a majority of the population of children that consume drinking water. The results of the 1994-96 CSFII analysis indicate that for children from 1 to 10 years of age, the arithmetic mean, 75th, and 90th percentile values are 0.4, 0.6, and 0.9 L/day, respectively (USEPA, 2000a). The 1 L/day value represents the 93rd percentile for this group. The arithmetic mean, 75th, and 90th percentile values for smaller children, ages 1 to 3 years, are 0.3, 0.5, and 0.7 L/day, respectively. The 1 L/day value represents the 97th percentile of the group ages 1 to 3 years old. For the category of infants under 1 year of age, the arithmetic mean, 75th, and 90th percentile values are 0.3, 0.7, and 0.9 L/day, respectively. These data can similarly be compared to those of the older National Cancer Institute (NCI) study. The arithmetic mean, 75th, and 90th percentile values for children 1 to 10 years old were 0.74, 0.96, and 1.3 L/day,

respectively. The mean, 75th, and 90th percentile values for children 1 to 3 years old in the NCI study were 0.6, 0.8, and 1.2 L/day, respectively. Finally, the mean, 75th, and 90th percentile values for infants less than 6 months old were 0.3, 0.3, and 0.6 L/day, respectively (Ershow and Cantor, 1989).

4.3.2.3 Rates Based on Combining Drinking Water Intake and Body Weight

As an alternative to considering body weight and drinking water intake rates separately, EPA is providing rates based on intake per unit body weight data (in units of ml/kg) in the Exposure Assessment TSD, with additional discussion on their use. These rates are based on self-reported body weights from the CSFII survey respondents for the 1994-96 data. While EPA intends to derive or revise national default criteria on the separate intake values and body weights, in part due to the strong input received from its State stakeholders, the ml/kg-BW/day values are provided in the TSD for States or authorized Tribes that prefer their use. It should be noted that in their 1993 review, EPA's Science Advisory Board (SAB) felt that using drinking water intake rate assumptions on a per unit body weight basis would be more accurate, but did not believe this change would appreciably affect the criteria values (USEPA, 1993).

4.3.3 Fish Intake Rates

The basis for the fish intake rates is the 1994-96 CSFII conducted by the USDA, and described above in Section 4.3.2.

4.3.3.1 Rates Protective of Human Health from Chronic Exposure

EPA recommends a default fish intake rate of 17.5 grams/day to adequately protect the general population of fish consumers, based on the 1994 to 1996 data from the USDA's CSFII Survey. EPA will use this value when deriving or revising its national 304(a) criteria. This value represents the 90th percentile of the 1994-96 CSFII data. This value also represents the uncooked weight estimated from the CSFII data, and represents intake of freshwater and estuarine finfish and shellfish only. For deriving AWQC, EPA has also considered the States' and Tribes' needs to provide adequate protection from adverse health effects to highly exposed populations such as recreational and subsistence fishers, in addition to the general population. Based on available studies that characterize consumers of fish, recreational fishers and subsistence fishers are two distinct groups whose intake rates may be greater than the general population. It is, therefore, EPA's decision to discuss intakes for these two groups, in addition to the general population.

EPA recommends default fish intake rates for recreational and subsistence fishers of 17.5 grams/day and 142.4 grams/day, respectively. These rates are also based on uncooked weights for fresh/estuarine finfish and shellfish only. However, because the level of fish intake in highly exposed populations varies by geographical location, EPA suggests a four preference hierarchy for States and authorized Tribes to follow when deriving consumption rates that encourages use of the best local, State, or regional data available. A thorough discussion of the development of this policy method and relevant data sources is contained in the Exposure Assessment TSD. The hierarchy is also presented here because EPA strongly emphasizes that States and authorized

Tribes should consider developing criteria to protect highly exposed population groups and use local or regional data over the default values as more representative of their target population group(s). The four preference hierarchy is: (1) use of local data; (2) use of data reflecting similar geography/population groups; (3) use of data from national surveys; and (4) use of EPA's default intake rates.

The recommended four preference hierarchy is intended for use in evaluating fish intake from fresh and estuarine species only. Therefore, to protect humans who additionally consume marine species of fish, the marine portion should be considered an *other source of exposure* when calculating an RSC for dietary intake. Refer to the Exposure Assessment TSD for further discussion. States and Tribes need to ensure that when evaluating overall exposure to a contaminant, marine fish intake is not double-counted with the other dietary intake estimate used. Coastal States and authorized Tribes that believe accounting for total fish consumption (i.e., fresh/estuarine and marine species) is more appropriate for protecting the population of concern may do so, provided that the marine intake component is not double-counted with the RSC estimate. Tables of fish consumption intakes based on the CSFII in the TSD provide rates for fresh/estuarine species, marine species, and total (combined) values to facilitate this option for States and Tribes. Throughout this section, the terms "fish intake" or "fish consumption" are used. These terms refer to the consumption of finfish and shellfish, and the CSFII survey includes both. States and Tribes should ensure that when selecting local or regionally-specific studies, both finfish and shellfish are included when the population exposed are consumers of both types.

EPA's first preference is that States and authorized Tribes use the results from fish intake surveys of local watersheds within the State or Tribal jurisdiction to establish fish intake rates that are representative of the defined populations being addressed for the particular waterbody. Again, EPA recommends that data indicative of fresh/estuarine species only be used which is, by and large, most appropriate for developing AWQC. EPA also recommends the use of uncooked weight intake values, which is discussed in greater detail with the fourth preference. States and authorized Tribes may use either high-end values (such as the 90^{th} or 95^{th} percentile values) or average values for an identified population that they plan to protect (e.g., subsistence fishers, sport fishers, or the general population). EPA generally recommends that arithmetic mean values should be the lowest value considered by States or Tribes when choosing intake rates for use in criteria derivation. When considering geometric mean (median) values from fish consumption studies, States and authorized Tribes need to ensure that the distribution is based on survey respondents who reported consuming fish because surveys based on both consumers and nonconsumers can often result in median values of zero. If a State or Tribe chooses values (whether the central tendency or high-end values) from studies that particularly target high-end consumers, these values should be compared to high-end fish intake rates for the general population to make sure that the high-end consumers within the general population would be protected by the chosen intake rates. EPA believes this is a reasonable procedure and is also consistent with the recent Great Lakes Water Quality Initiative (known as the "GLI") (USEPA, 1995). States and authorized Tribes may wish to conduct their own surveys of fish intake, and EPA guidance is available on methods to conduct such studies in *Guidance for Conducting Fish and Wildlife Consumption Surveys* (USEPA, 1998). Results from broader geographic regions in which the State or Tribe is located can also be used, but may not be as applicable as results from

local watersheds. Since such studies would ultimately form the basis of a State or Tribe's AWQC, EPA would review any surveys of fish intake for consistency with the principles of EPA's guidance as part of the Agency's review of water quality standards under Section 303(c).

If surveys conducted in the geographic area of the State or Tribe are not available, EPA's second preference is that States and authorized Tribes consider results from existing fish intake surveys that reflect similar geography and population groups (e.g., from a neighboring State or Tribe or a similar watershed type), and follow the method described above regarding target values to derive a fish intake rate. Again, EPA recommends the use of uncooked weight intake values and the use of fresh/estuarine species data only. Results of existing local and regional surveys are discussed in greater detail in the TSD.

If applicable consumption rates are not available from local, State, or regional surveys, EPA's third preference is that States and authorized Tribes select intake rate assumptions for different population groups from national food consumption surveys. EPA has analyzed one such national survey, the 1994-96 CSFII. As described in Section 4.3.2, this survey, conducted annually by the USDA, collects food consumption information from a probability sample of the population of all 50 states. Respondents to the survey provide two days of dietary recall data. A detailed description of the combined 1994-96 CSFII survey, the statistical methodology, and the results and uncertainties of the EPA analyses are provided in a separate EPA report (USEPA, 2000b). The Exposure Assessment TSD for this Methodology presents selected results from this report including point and interval estimates of combined finfish and shellfish consumption for the mean, 50^{th} (median), 90^{th}, 95^{th}, and 99^{th} percentiles. The estimated fish consumption rates are by fish habitat (i.e., freshwater/estuarine, marine and all habitats) for the following population groups: (1) all individuals; (2) individuals age 18 and over; (3) women ages 15-44; and (4) children age 14 and under. Three kinds of estimated fish consumption rates are provided: (1) per capita rates (i.e., rates based on consumers and nonconsumers of fish from the survey period– refer to the TSD for further discussion); (2) consumers-only rates (i.e., rates based on respondents who reported consuming finfish or shellfish during the two-day reporting period); and (3) per capita consumption by body weight (i.e., per capita rates reported as milligrams of fish per kilogram of body weight per day).

EPA's fourth preference is that States and authorized Tribes use as fish intake assumptions the following default rates, based on the 1994-96 CSFII data, that EPA believes are representative of fish intake for different population groups: 17.5 grams/day for the general adult population and sport fishers, and 142.4 grams/day for subsistence fishers. These are risk management decisions that EPA has made after evaluating numerous fish intake surveys. These values represent the uncooked weight intake of freshwater/estuarine finfish and shellfish. As with the other preferences, EPA requests that States and authorized Tribes routinely consider whether there is a substantial population of sport fishers or subsistence fishers when developing site-specific estimates, rather than automatically basing them on the typical individual. Because the combined 1994-96 CSFII survey is national in scope, EPA will use the results from this survey to estimate fish intake for deriving national criteria. EPA has recognized the data gaps and uncertainties associated with the analysis of the 1994-96 CSFII survey in the process of making its default recommendations. The estimated mean of freshwater and estuarine fish ingestion for adults is 7.50 grams/day, and the median is 0 grams/day. The estimated 90^{th}

percentile is 17.53 grams/day; the estimated 95th percentile is 49.59 grams/day; and the estimated 99th percentile is 142.41 grams/day. The median value of 0 grams/day may reflect the portion of individuals in the population who never eat fish as well as the limited reporting period (2 days) over which intake was measured. By applying as a default 17.5 grams/day for the general adult population, EPA intends to select an intake rate that is protective of a majority of the population (again, the 90th percentile of consumers and nonconsumers according to the 1994-96 CSFII survey data). Trophic level breakouts are: TL2 = 3.8 grams/day; TL3 = 8.0 grams/day; and TL4 = 5.7 grams/day. EPA further considers 17.5 grams/day to be indicative of the average consumption among sport fishers based on averages in the studies reviewed, which are presented in the Exposure Assessment TSD. Similarly, EPA believes that the assumption of 142.4 grams/day is within the range of average consumption estimates for subsistence fishers based on the studies reviewed. Experts at the 1992 National Workshop that initiated the effort to revise this Methodology acknowledged that the national survey high-end values are representative of average rates for highly exposed groups such as subsistence fishermen, specific ethnic groups, or other highly exposed people. EPA is aware that some local and regional studies indicate greater consumption among Native American, Pacific Asian American, and other subsistence consumers, and recommends the use of those studies in appropriate cases, as indicated by the first and second preferences. Again, States and authorized Tribes have the flexibility to choose intake rates higher than an average value for these population groups. If a State or authorized Tribe has not identified a separate well-defined population of high-end consumers and believes that the national data from the 1994-96 CSFII are representative, they may choose these recommended rates.

As indicated above, the default intake values are based on the uncooked weights of the fish analyzed. There has been some question regarding whether to use cooked or uncooked weights of fish intake for deriving the AWQC. Studies show that, typically, with a filet or steak of fish, the weight loss in cooking is about 20 percent; that is, the uncooked weight is approximately 20 percent higher (Jacobs et al., 1998). This obviously means that using uncooked weights results in a slightly higher intake rate and slightly more stringent AWQC. In researching consumption surveys for this proposal, EPA has found that some surveys have reported rates for cooked fish, others have reported uncooked rates, and many more are unclear as to whether cooked or uncooked rates are used. The basis of the CSFII survey was prepared or *as consumed* intakes; that is, the survey respondents estimated the weight of fish that they consumed. This was also true with the GLI (which was specifically based on studies describing consumption rates of cooked fish) and, by and large, cooked fish is what people consume. However, EPA's *Guidance For Assessing Chemical Contaminant Data For Use In Fish Advisories* recommends analysis and advisories based on uncooked fish (USEPA, 1997a). EPA considered the potential confusion over the fact that the uncooked weights are used in the fish advisory program. Further, the measures of a contaminant in fish tissue samples that are applicable to compliance monitoring and the permitting program are related to the uncooked weights. The choice of intakes is also complicated by factors such as the effect of the cooking process, the different parts of a fish where a chemical may accumulate, and the method of preparation.

After considering all of the above (in addition to public input received), EPA will derive its national default criteria based on the uncooked weight fish intakes. The Exposure

Assessment TSD provides additional guidance on site-specific modifications. Specifically, an alternate approach is described for calculating AWQC with the *as consumed* weight–which is more directly associated with human exposure and risk–and then adjusting the value by the approximate 20 percent loss to an uncooked equivalent (thereby representing the same relative risk as the *as consumed* value). This approach results in a different AWQC value (than using the uncooked weights) and represents a more direct translation of the *as consumed* risk to the uncooked equivalent. However, EPA understands that it is more scientifically rigorous and may be too intensive of a process for States and Tribes to rely on. The option is presented in the TSD to offer States and authorized Tribes greater flexibility with their water quality standards program.

The default fish intake values also reflect specific designations of species classified in accordance with information regarding the life history of the species or based on landings information form the National Marine Fisheries Service. Most significantly, salmon has been reclassified from a freshwater/estuarine species to a marine species. As marine harvested salmon represents approximately 99 percent of salmon consumption in the 1994-96 CSFII Survey, removal reduces the overall fresh/estuarine fish consumption rate by 13 percent. Although they represent a very small percentage of freshwater/estuarine intake, land-locked and farm-raised salmon consumed by 1994-96 CSFII respondents are still included. The rationale for the default intake species designations is explained in the Exposure Assessment TSD. Once again, EPA emphasizes the flexibility for States and authorized Tribes to use alternative assumptions based on local or regional data to better represent their population groups of concern.

4.3.3.2 Rates Protective of Developmental Human Health Effects

Exposures resulting in health effects in children or developmental effects in fetuses may be of primary concern. As discussed at the beginning of this section on exposure factors used, in a situation where acute or sub-chronic toxicity and exposure are the basis of an RfD (or POD/UF), EPA will consider basing its national default criteria on children or women of childbearing age, depending on the target population at greatest risk. EPA recommends that States and authorized Tribes use exposure factors for children or women of childbearing age in these situations. As stated previously, EPA is not recommending the development of additional AWQC but is acknowledging that basing a criterion on these population groups is a potential course of action and is, therefore, recommending the following default intake rates for such situations.

EPA's preferences for States and authorized Tribes in selecting values for intake rates relevant for children is the same as that discussed above for establishing values for average daily consumption rates for chronic effects; i.e., in decreasing order of preference, results from fish intake surveys of local watersheds, results from existing fish intake surveys that reflect similar geography and population groups, the distribution of intake rates from nationally based surveys (e.g., the CSFII), or lastly, the EPA default rates. When an RfD is based on health effects in children, EPA recommends a default intake rate of 156.3 grams/day for assessing those contaminants that exhibit adverse effects. This represents the 90th percentile consumption rate for actual consumers of freshwater/estuarine finfish and shellfish for children ages 14 and under using the combined 1994 to 1996 results from the CSFII survey. The value was calculated based

on data for only those children who ate fish during the 2-day survey period, and the intake was averaged over the number of days during which fish was actually consumed. EPA believes that by selecting the data for consumers only, the 90th percentile is a reasonable intake rate to approximate consumption of fresh/estuarine finfish and shellfish within a short period of time for use in assessments where adverse effects in children are of primary concern. As discussed previously, EPA will use a default body weight of 30 kg to address potential acute or subchronic effects from fish consumption by children. EPA is also providing these default intake values for States and authorized Tribes that choose to provide additional protection when developing criteria that they believe should be based on health effects in children. This is consistent with the rationale in the recent GLI (USEPA, 1995) and is an approach that EPA believes is reasonable. Distributional information on intake values relevant for assessing exposure when health effects to children are of concern is presented in the Exposure Assessment TSD.

There are also cases in which pregnant women may be the population of most concern, due to the possibility of developmental effects that may result from exposures of the mother to toxicants. In these cases, fish intake rates specific to females of childbearing age are most appropriate when assessing exposures to developmental toxicants. When an RfD is based on developmental toxicity, EPA proposes a default intake rate of 165.5 grams/day for assessing exposures for women of childbearing age from contaminants that cause developmental effects. This is equivalent to the 90th percentile consumption rate for actual consumers of freshwater/ estuarine finfish and shellfish for women ages 15 to 44 using the combined 1994 to1996 results from the CSFII survey. As with the rate for children, this value represents only those women who ate fish during the 2-day survey period. As discussed previously, EPA will use a default body weight of 67 kg for women of childbearing age.

4.3.3.3 Rates Based on Combining Fish Intake and Body Weight

As with the drinking water intake values, EPA is providing values for fish intake based on a per unit body weight basis (in units of mg/kg) in the Exposure Assessment TSD. These rates use the self-reported body weights of the 1994-96 CSFII survey. Again, while EPA intends to derive or revise national default criteria on the separate intake values and body weights, the mg/kg-BW/day values are provided in the TSD for States or authorized Tribes that prefer their use.

4.4 REFERENCES FOR EXPOSURE

Ershow A.G., Brown L.M. and Cantor K.P. 1991. Intake of tapwater and total water by pregnant and lactating women. *Am. J. Public Health.* 81:328-334.

Ershow A.G. and K.P. Cantor. 1989. *Total Water and Tap Water Intake in the United States: Population-based Estimates of Quantities and Sources*. National Cancer Institute. Bethesda, MD. Order #263-MD-810264.

Gibbons, J.D. 1971. *Nonparametric Statistical Inference.* Chapter 2: Order Statistics. McGraw-Hill, Inc. New York, NY.

Jacobs, H.L., H.D. Kahn, K.A. Stralka, and D.B. Phan. 1998. Estimates of per capita fish consumption in the U.S. based on the continuing survey of food intake by individuals (CSFII). *Risk Analysis: An International Journal* 18(3).

McDowell, M. 2000. Personal communication between Denis R. Borum, U.S. Environmental Protection Agency, and Margaret McDowell, Health Statistician, National Health and Nutrition Examination Survey, National Center for Health Statistics. March 24, 2000.

USDA. 1998. U.S. Department of Agriculture. *1994–1996 Continuing Survey of Food Intakes by Individuals and 1994–1996 Diet and Health Knowledge Survey*. Agricultural Research Service, USDA. NTIS CD–ROM, accession number PB98–500457. [Available from the National Technical Information Service, 5285 Port Royal Road, Springfield, VA 22161. Phone: (703) 487–4650.]

USEPA. 1993. *Review of the Methodology for Developing Ambient Water Quality Criteria for the Protection of Human Health.* Prepared by the Drinking Water Committee of the Science Advisory Board. EPA-SAB-DWC

USEPA. 1994. Reference dose (RfD) for oral exposure for cadmium. *Integrated Risk Information System (IRIS). Online.* (Verification date 02/01/94.) Office of Health and Environmental Assessment, Environmental Criteria and Assessment Office. Cincinnati, OH.

USEPA. 1995. *Great Lakes Water Quality Initiative Technical Support Document for the Procedure to Determine Bioaccumulation Factors*. Office of Water. Washington, DC. EPA/820/B-95/005.

USEPA. 1997a. *Guidance for Assessing Chemical Contaminant Data for Use in Fish Advisories. Volume II: Risk Assessment and Fish Consumption Limits*. Second Edition. Office of Water. Washington DC. EPA/823/B-97/009.

USEPA. 1997b. *Exposure Factors Handbook*. National Center for Environmental Assessment, Office of Research and Development. Washington, DC. EPA/600/P-95/002Fa. August.

USEPA. 1998. *Guidance for Conducting Fish and Wildlife Consumption Surveys*. Office of Science and Technology, Office of Water. Washington, DC. EPA-823-B-98-007. November.

USEPA. 2000a. *Estimated Per Capita Water Ingestion in the United States: Based on Data Collected by the United States Department of Agriculture's 1994-96 Continuing Survey of Food Intakes by Individuals.* Office of Science and Technology, Office of Water. Washington, DC. EPA-822-00-008. April.

USEPA. 2000b. *Estimated Per Capita Fish Consumption in the United States: Based on Data Collected by the United States Department of Agriculture's 1994-1996 Continuing*

Survey of Food Intake by Individuals. Office of Science and Technology, Office of Water, Washington, DC. March.

WESTAT. 2000. *Memorandum on Body Weight Estimates Based on NHANES III data, Including Data Tables and Graphs*. Analysis conducted and prepared by WESTAT, under EPA Contract No. 68-C-99-242. March 3, 2000.

5. BIOACCUMULATION

5.1 INTRODUCTION

Aquatic organisms can accumulate certain chemicals in their bodies when exposed to these chemicals through water, their diet, and other sources. This process is called bioaccumulation. The magnitude of bioaccumulation by aquatic organisms varies widely depending on the chemical but can be extremely high for some highly persistent and hydrophobic chemicals. For such highly bioaccumulative chemicals, concentrations in aquatic organisms may pose unacceptable human health risks from fish and shellfish consumption even when concentrations in water are too low to cause unacceptable health risks from drinking water consumption alone. These chemicals may also biomagnify in aquatic food webs, a process whereby chemical concentrations increase in aquatic organisms of each successive trophic level due to increasing dietary exposures (e.g., increasing concentrations from algae, to zooplankton, to forage fish, to predatory fish).

In order to prevent harmful exposures to waterborne chemicals through the consumption of contaminated fish and shellfish, national 304(a) water quality criteria for the protection of human health must address the process of chemical bioaccumulation in aquatic organisms. For deriving national 304(a) criteria to protect human health, EPA accounts for potential bioaccumulation of chemicals in fish and shellfish through the use of national bioaccumulation factors (BAFs). A national BAF is a ratio (in L/kg) that relates the concentration of a chemical in water to its expected concentration in commonly consumed aquatic organisms in a specified trophic level. An illustration of how national BAFs are used in the derivation of 304(a) criteria for carcinogens using linear low-dose extrapolation is shown in the following equation:

$$AWQC = RSD \bullet \left(\frac{BW}{DI + \sum_{i=2}^{4} (FI_i \bullet BAF_i)} \right) \qquad \text{(Equation 5-1)}$$

where:

RSD	=	Risk specific dose (mg/kg-day)
BW	=	Human body weight (kg)
DI	=	Drinking water intake (L/day)
FI_i	=	Fish intake at trophic level I, where I=2, 3, and 4;
BAF_i	=	National bioaccumulation factor at trophic level I, where I=2, 3, and 4

The purpose of this chapter is to present EPA's recommended methodology for deriving national bioaccumulation factors for setting national 304(a) water quality criteria to protect human health. A detailed scientific basis of the recommended national BAF methodology is provided in the Bioaccumulation TSD. While the methodology detailed in this chapter is

intended to be used by EPA for deriving national BAFs, EPA encourages States and authorized Tribes to derive BAFs that are specific to certain regions or waterbodies, where appropriate. Guidance to States and authorized Tribes for deriving site-specific BAFs is provided in the Biaccumulation TSD.

5.1.1 Important Bioaccumulation and Bioconcentration Concepts

Several attributes of the bioaccumulation process are important to understand when deriving national BAFs for use in setting national 304(a) criteria. First, the term "bioaccumulation" refers to the uptake and retention of a chemical by an aquatic organism from all surrounding media (e.g., water, food, sediment). The term "bioconcentration" refers to the uptake and retention of a chemical by an aquatic organism from water only. For some chemicals (particularly those that are highly persistent and hydrophobic), the magnitude of bioaccumulation by aquatic organisms can be substantially greater than the magnitude of bioconcentration. Thus, an assessment of bioconcentration alone would underestimate the extent of accumulation in aquatic biota for these chemicals. Accordingly, EPA's guidelines presented in this chapter emphasize the measurement of chemical bioaccumulation by aquatic organisms, whereas EPA's 1980 Methodology emphasized the measurement of bioconcentration.

Another noteworthy aspect of bioaccumulation process is the issue of steady-state conditions. Specifically, both bioaccumulation and bioconcentration can be viewed simply as the result of competing rates of chemical uptake and depuration (chemical loss) by an aquatic organism. The rates of chemical uptake and depuration can be affected by various factors including the properties of the chemical, the physiology of the organism in question, water quality and other environmental conditions, ecological characteristics of the waterbody (e.g., food web structure), and the concentration and loadings history of the chemical. When the rates of chemical uptake and depuration are equal, tissue concentrations remain constant over time and the distribution of the chemical between the organism and its source(s) is said to be at steady-state. For constant chemical exposures and other conditions, the steady-state concentration in the organism represents the highest accumulation potential of the chemical in that organism under those conditions. The time required for a chemical to achieve steady state has been shown to vary according to the properties of the chemical and other factors. For example, some highly hydrophobic chemicals can require long periods of time to reach steady state between environmental compartments (e.g., many months), while highly hydrophilic chemicals usually reach steady-state relatively quickly (e.g., hours to days).

Since national 304(a) criteria for the protection of human health are typically designed to protect humans from harmful lifetime or long-term exposures to waterborne contaminants, the assessment of bioaccumulation that equals or approximates steady-state accumulation is one of the principles underlying the derivation of national BAFs. For some chemicals that require relatively long periods of time to reach steady-state in tissues of aquatic organisms, changes in water column concentrations may occur on a much more rapid time scale compared to the corresponding changes in tissue concentrations. Thus, if the system departs substantially from steady-state conditions and water concentrations are not averaged over a sufficient time period, the ratio of the tissue concentration to a water concentration may have little resemblance to the steady-state ratio and have little predictive value of long-term bioaccumulation potential.

Therefore, BAF measurements should be based on water column concentrations which are averaged over a sufficient period of time (e.g., a duration comparable to the time required for the chemical to reach steady-state). In addition, BAF measurements should be based on adequate spatial averaging of both tissue and water column concentrations for use in deriving 304(a) criteria for the protection of human health.

For this reason, a BAF is defined in this Methodology as representing the ratio (in L/kg-tissue) of a concentration of a chemical in tissue to its concentration in the surrounding water in situations where the organism and its food are exposed and the ratio does not change substantially over time (i.e., the ratio which reflects bioaccumulation at or near steady-state). A bioconcentration factor (BCF) is the ratio (in L/kg-tissue) of the concentration of a substance in tissue of an aquatic organism to its concentration in the ambient water, in situations where the organism is exposed through the water only and the ratio does not change substantially over time.

5.1.2 Goal of the National BAF

The goal of EPA's national BAF is to represent the long-term, average bioaccumulation potential of a chemical in edible tissues of aquatic organisms that are commonly consumed by humans throughout the United States. National BAFs are not intended to reflect fluctuations in bioaccumulation over short time periods (e.g., a few days) because 304(a) human health criteria are generally designed to protect humans from long-term exposures to waterborne chemicals. National BAFs are also intended to account for some major chemical, biological, and ecological attributes that can affect bioaccumulation in bodies of water across the United States. For example, separate procedures are provided for deriving national BAFs depending on the type of chemical (i.e., nonionic organic, ionic organic, inorganic and organometallic). In addition, EPA's national BAFs are derived separately for each trophic level to account for potential biomagnification of some chemicals in aquatic food webs and broad physiological differences between trophic levels that may influence bioaccumulation. Because lipid content of aquatic organisms and the amount of organic carbon in the water column have been shown to affect bioaccumulation of nonionic organic chemicals, EPA's national BAFs are adjusted to reflect the lipid content of commonly consumed fish and shellfish and the freely dissolved fraction of the chemical in ambient water for these chemicals.

5.1.3 Changes to the 1980 Methodology

Numerous scientific advances have occurred in the area of bioaccumulation since the publication of the 1980 Methodology for deriving AWQC for the protection of human health (USEPA, 1980). These advances have significantly increased our ability to assess and predict the bioaccumulation of chemicals in aquatic biota. As a result, EPA has revised the bioaccumulation portion of the 1980 Methodology to reflect the current state of the science and to improve accuracy in assessing bioaccumulation for setting 304(a) criteria for the protection of human health. The changes contained in the bioaccumulation portion of the 2000 Human Health Methodology are mostly designed to:

- Improve the ability to incorporate chemical exposure from sediments and aquatic food webs in assessing bioaccumulation potential,

- Expand the ability to account for site-specific factors which affect bioaccumulation, and

- Incorporate new data and assessment tools into the bioaccumulation assessment process.

A summary of the key changes that have been incorporated into the bioaccumulation portion of the 2000 Human Health Methodology and appropriate comparisons to the1980 Methodology are provided below.

5.1.3.1 Overall Approach

The 1980 Methodology for deriving 304(a) criteria for the protection of human health emphasized the assessment of bioconcentration (uptake from water only) through the use of the BCF. Based on the 1980 Methodology, measured BCFs were usually determined from laboratory data unless field data demonstrated consistently higher or lower accumulation compared with laboratory data. In these cases, "field BCFs" (currently termed field-measured BAFs) were recommended for use. For lipophilic chemicals where lab or field-measured data were unavailable, EPA recommended predicting BCFs from the octanol-water partition coefficient and the following equation from Veith et al. (1979): "log BCF = (0.85 log K_{ow}) - 0.70".

The 2000 Human Health Methodology revisions contained in this chapter emphasize the measurement of bioaccumulation (uptake from water, sediment, and diet) through the use of the BAF. Consistent with the 1980 Methodology, measured data are preferred over predictive approaches for determining the BAF (i.e., field-measured BAFs are generally preferred over predicted BAFs). However, the 2000 Human Health Methodology contains additional methods for deriving a national BAF that were not available in 1980. The preference for using the BAF methods also differs depending on the type and properties of the chemical. For example, the BAF derivation procedure differs for each of three broadly defined chemical categories: (1) nonionic organic, (2) ionic organic, and (3) inorganic and organometallic chemicals. Furthermore, within the category of nonionic organic chemicals, different procedures are used to derive the BAF depending on a chemicals' hydrophobicity and extent of chemical metabolism that would be expected to occur in aquatic biota.

5.1.3.2 Lipid Normalization

In the 1980 Methodology, BCFs for lipophilic chemicals were normalized by the lipid fraction in the tissue of fish and shellfish used to determine the BCF. Lipid normalization enabled BCFs to be averaged across tissues and organisms. Once the average lipid-normalized BCF was determined, it was adjusted by the consumption-weighted lipid content of commonly consumed aquatic organisms in the United States to obtain an overall consumption-weighted BCF. A similar procedure has been retained in the 2000 Human Health Methodology, whereby BAFs for nonionic organic chemicals are lipid normalized and adjusted by the consumption-weighted lipid content of commonly consumed organisms to obtain a BAF for criteria

calculations. However, the 2000 Human Health Methodology uses more up-to-date lipid data and consumption data for deriving the consumption-weighted BAFs.

5.1.3.3 Bioavailability

Bioconcentration factors derived according to the 1980 Methodology were based on the total concentration of the chemical in water, for both lipophilic and nonlipophilic chemicals. In the 2000 Human Health Methodology, BAFs for nonionic organic chemicals are derived using the most bioavailable fraction (i.e., the freely dissolved fraction) to account for the influence of particulate and dissolved organic carbon on a chemical's bioavailability. Such BAFs are then adjusted to reflect the expected bioavailability at the sites of interest (i.e., by adjusting for organic carbon concentrations at the sites of interest). Procedures for accounting for the effect of organic carbon on bioaccumulation were published previously by EPA under the Great Lakes Water Quality Initiative (GLWQI or GLI) rulemaking (USEPA, 1995a,b). Bioavailability is also considered in developing BAFs for the other chemical classes defined in the 2000 Human Health Methodology (e.g., ionic organics, inorganics/organometallics) but is done so on a chemical-by-chemical basis.

5.1.3.4 Trophic Level Considerations

In the 1980 Methodology, BCFs were determined and used for criteria derivation without explicit regard to the trophic level of the aquatic organism (e.g., benthic filter feeder, forage fish, predatory fish). Over the past two decades, much information has been assembled which demonstrates that an organism's trophic position in the aquatic food web can have an important effect on the magnitude of bioaccumulation of certain chemicals. In order to account for the variation in bioaccumulation that is due to trophic position of the organism, the 2000 Human Health Methodology recommends that BAFs be determined and applied on a trophic level-specific basis.

5.1.3.5 Site-Specific Adjustments

The 1980 Methodology contained little guidance for making adjustments to the national BCFs to reflect site- or region-specific conditions. The 2000 Human Health Methodology has greatly expanded the guidance to States and authorized Tribes for making adjustments to national BAFs to reflect local conditions. This guidance is contained in the Bioaccumulation TSD. In the Bioaccumulation TSD, guidance and data are provided for adjusting national BAFs to reflect the lipid content in locally consumed aquatic biota and the organic carbon content in the waterbodies of concern. This guidance also allows the use of appropriate bioaccumulation models for deriving site-specific BAFs. EPA also plans to publish detailed guidance on designing and conducting field bioaccumulation studies for measuring BAFs and biota-sediment accumulation factors (BSAFs). In general, EPA encourages States and authorized Tribes to make site-specific modifications to EPA's national BAFs provided such adjustments are scientifically defensible and adequately protect the designated use of the waterbody.

While the aforementioned revisions are new to EPA's Methodology for deriving national 304(a) criteria for the protection of human health, many of these refinements have been

incorporated in prior Agency guidance and regulations. For example, the use of food chain multipliers to account for the biomagnification of nonionic organic chemicals in aquatic food webs when measured data are unavailable was introduced by EPA in three documents*: Technical Support Document for Water Quality-Based Toxics Control* (USEPA, 1991), a draft document entitled *Assessment and Control of Bioconcentratable Contaminants in Surface Waters* (USEPA, 1993), and in the *Great Lakes Water Quality Initiative* (GLI) (USEPA, 1995b). Similarly, procedures for predicting BAFs using BSAFsand incorporating the effect of organic carbon on bioavailability were used to derive water quality criteria under the GLI.

5.1.4 Organization of This Section

The methodology for deriving national BAFs for use in deriving National 304(a) Human Health AWQC is provided in the following sections. Important terms used throughout this chapter are defined in Section 5.2. Section 5.3 provides an overview of the BAF derivation guidelines. Detailed procedures for deriving national BAFs are provided in Section 5.4 for nonionic organic chemicals, in Section 5.5 for ionic organic chemicals, and in Section 5.6 for inorganics and organometallic chemicals. Literature cited is provided in Section 5.7.

5.2 DEFINITIONS

The following terms and definitions are used throughout this chapter.

Bioaccumulation. The net accumulation of a substance by an organism as a result of uptake from all environmental sources.

Bioconcentration. The net accumulation of a substance by an aquatic organism as a result of uptake directly from the ambient water, through gill membranes or other external body surfaces.

Bioaccumulation Factor (BAF). The ratio (in L/kg-tissue) of the concentration of a substance in tissue to its concentration in the ambient water, in situations where both the organism and its food are exposed and the ratio does not change substantially over time. The BAF is calculated as:

$$BAF = \frac{C_t}{C_w} \qquad \text{(Equation 5-2)}$$

where:

C_t = Concentration of the chemical in the specified wet tissue
C_w = Concentration of chemical in water

Bioconcentration Factor (BCF). The ratio (in L/kg-tissue) of the concentration of a substance in tissue of an aquatic organism to its concentration in the ambient water, in situations where the organism is exposed through the water only and the ratio does not change substantially over time. The BCF is calculated as:

$$BCF = \frac{C_t}{C_w} \qquad \text{(Equation 5-3)}$$

where:

C_t = Concentration of the chemical in the specified wet tissue
C_w = Concentration of chemical in water

Baseline BAF (BAF_ℓ^{fd}). For nonionic organic chemicals (and certain ionic organic chemicals where similar lipid and organic carbon partitioning behavior applies), a BAF (in L/kg-lipid) that is based on the concentration of freely dissolved chemical in the ambient water and the lipid normalized concentration in tissue.

Baseline BCF (BCF_ℓ^{fd}). For nonionic organic chemicals (and certain ionic organic chemicals where similar lipid and organic carbon partitioning behavior applies), a BCF (in L/kg-lipid) that is based on the concentration of freely dissolved chemical in the ambient water and the lipid normalized concentration in tissue.

Biomagnification. The increase in tissue concentration of a chemical in organisms at successive trophic levels through a series of predator-prey associations, primarily through the mechanism of dietary accumulation.

Biomagnification Factor (BMF). The ratio (unitless) of the tissue concentration of a chemical in a predator at a particular trophic level to the tissue concentration in its prey at the next lower trophic level for a given waterbody and chemical exposure. For nonionic organic chemicals (and certain ionic organic chemicals where similar lipid and organic carbon partitioning behavior applies), a BMF can be calculated using lipid-normalized concentrations in the tissue of organisms at two successive trophic levels as:

$$BMF_{(TL,\ n)} = \frac{C_{\ell\ (TL,\ n)}}{C_{\ell\ (TL,\ n-1)}} \qquad \text{(Equation 5-4)}$$

where:

$C_{\ell\ (TL,\ n)}$ = Lipid-normalized concentration in appropriate tissue of predator organism at a given trophic level (TL “n”)

$C_{\ell\ (TL,\ n-1)}$ = Lipid-normalized concentration in appropriate tissue of prey organism at the next lower trophic level from the predator (TL "n-1")

For inorganic, organometallic, and certain ionic organic chemicals where lipid and organic carbon partitioning does not apply, a BMF can be calculated using chemical concentrations in the tissue of organisms at two successive trophic levels as:

$$BMF_{(TL,\ n)} = \frac{C_{t\ (TL,\ n)}}{C_{t\ (TL,\ n-1)}} \qquad \text{(Equation 5-5)}$$

where:

$C_{t\ (TL,\ n)}$ = Concentration in appropriate tissue of predator organism at trophic level "n" (may be either wet weight or dry weight concentration so long as both the predator and prey concentrations are expressed in the same manner)

$C_{t\ (TL,\ n-1)}$ = Concentration in appropriate tissue of prey organism at the next lower trophic level from the predator (may be either wet weight or dry weight concentration so long as both the predator and prey concentrations are expressed in the same manner)

Biota-Sediment Accumulation Factor (BSAF). For nonionic organic chemicals (and certain ionic organic chemicals where similar lipid and organic carbon partitioning behavior applies), the ratio of the lipid-normalized concentration of a substance in tissue of an aquatic organism to its organic carbon-normalized concentration in surface sediment (expressed as kg of sediment organic carbon per kg of lipid), in situations where the ratio does not change substantially over time, both the organism and its food are exposed, and the surface sediment is representative of average surface sediment in the vicinity of the organism. The BSAF is defined as:

$$BSAF = \frac{C_{\ell}}{C_{soc}} \qquad \text{(Equation 5-6)}$$

where:

C_{ℓ} = The lipid-normalized concentration of the chemical in tissues of the biota (µg/g lipid)

C_{soc} = The organic carbon-normalized concentration of the chemical in the surface sediment (µg/g sediment organic carbon)

Depuration. The loss of a substance from an organism as a result of any active or passive process.

Food Chain Multiplier (FCM). For nonionic organic chemicals (and certain ionic organic chemicals where similar lipid and organic carbon partitioning behavior applies), the ratio of a baseline BAF_{ℓ}^{fd} for an organism of a particular trophic level to the baseline BCF_{ℓ}^{fd} (usually determined for organisms in trophic level one). For inorganic, organometallic, and certain ionic organic chemicals where lipid and organic carbon partitioning does not apply, a FCM is based on total (wet or dry weight) concentrations of the chemical in tissue.

Freely Dissolved Concentration. For nonionic organic chemicals, the concentration of the chemical that is dissolved in ambient water, excluding the portion sorbed onto particulate or dissolved organic carbon. The freely dissolved concentration is considered to represent the most bioavailable form of an organic chemical in water and, thus, is the form that best predicts bioaccumulation. The freely dissolved concentration can be determined as:

$$C_w^{fd} = (C_w^t) \cdot (f_{fd}) \qquad \text{(Equation 5-7)}$$

where:

C_w^{fd}	=	Freely dissolved concentration of the organic chemical in ambient water
C_w^t	=	Total concentration of the organic chemical in ambient water
f_{fd}	=	Fraction of the total chemical in ambient water that is freely dissolved

Hydrophilic. A term that refers to the extent to which a chemical is attracted to partitioning into the water phase. Hydrophilic organic chemicals have a greater tendency to partition into polar phases (e.g., water) compared to chemicals of hydrophobic chemicals.

Hydrophobic. A term that refers to the extent to which a chemical avoids partitioning into the water phase. Highly hydrophobic organic chemicals have a greater tendency to partition into nonpolar phases (e.g., lipid, organic carbon) compared with chemicals of lower hydrophobicity.

Lipid-normalized Concentration (C_{ℓ}). The total concentration of a contaminant in a tissue or whole organism divided by the lipid fraction in that tissue or whole organism. The lipid-normalized concentration can be calculated as:

$$C_{\ell} = \frac{C_t}{f_{\ell}} \qquad \text{(Equation 5-8)}$$

where:

C_t	=	Concentration of the chemical in the wet tissue (either whole organism or specified tissue)

f_ℓ = Fraction lipid content in the organism or specified tissue

Octanol-water Partition Coefficient (K_{ow}). The ratio of the concentration of a substance in the n-octanol phase to its concentration in the aqueous phase in an equilibrated two-phase octanol-water system. For log K_{ow}, the log of the octanol-water partition coefficient is a base 10 logarithm.

Organic Carbon-normalized Concentration (C_{soc}). For sediments, the total concentration of a contaminant in sediment divided by the fraction of organic carbon in sediment. The organic carbon-normalized concentration can be calculated as:

$$C_{soc} = \frac{C_s}{f_{oc}} \qquad \text{(Equation 5-9)}$$

where:

C_s = Concentration of chemical in sediment
f_{oc} = Fraction organic carbon in sediment

Uptake. Acquisition by an organism of a substance from the environment as a result of any active or passive process.

5.3 FRAMEWORK FOR DETERMINING NATIONAL BIOACCUMULATION FACTORS

5.3.1 Four Different Methods

Bioaccumulation factors used to derive national BAFs can be measured or predicted using some or all of the following four methods, depending on the type of chemical and its properties. These methods are:

(1) a measured BAF obtained from a field study (i.e., a field-measured BAF);

(2) a BAF predicted from a field-measured BSAF;

(3) a BAF predicted from a laboratory-measured BCF (with or without adjustment by an FCM); and

(4) a BAF predicted from a chemical's octanol-water partition coefficient (K_{ow}), with or without adjustment using an FCM.

A brief summary of each of the four methods is provided below. Additional details on the use of these four methods is provided in Section 5.4 (for nonionic organics), Section 5.5 (for ionic organics) and Section 5.6 (for inorganics and organometallics).

1. **Field-Measured BAF.** Use of a field-measured BAF, which is the most direct measure of bioaccumulation, is the only method that can be used to derive a national BAF for all types of chemicals (i.e., nonionic organic, ionic organic, and inorganic and organometallic chemicals). A field-measured BAF is determined from a field study using measured chemical concentrations in the aquatic organism and its surrounding water. Because field studies are conducted in natural aquatic ecosystems, a field-measured BAF reflects an organism's exposure to a chemical through all relevant exposure pathways (i.e., water, sediment, and diet). A field-measured BAF also reflects any metabolism of a chemical that might occur in the aquatic organism or its food web. Therefore, field-measured BAFs are appropriate for all chemicals, regardless of the extent of chemical metabolism in biota.

2. **Field-measured BSAF.** For nonionic organic chemicals (and certain ionic organic chemicals where similar lipid and organic carbon partitioning behavior applies), a BAF can also be predicted from BSAFs. A BSAF is similar to a field-measured BAF in that the concentration of a chemical in biota is measured in the field and reflects an organism's exposure to all relevant exposure routes. A BSAF also reflects any chemical metabolism that might occur in the aquatic organism or its food web. However, unlike a field-measured BAF which references the biota concentration to the water concentration, a BSAF references the biota concentration to the sediment concentration. Use of the BSAF procedure is restricted to organic chemicals which are classified as being moderately to highly hydrophobic.

3. **Lab-measured BCF.** A laboratory-measured BCF can also be used to estimate a BAF for organic and inorganic chemicals. However, unlike a field-measured BAF or a BAF predicted from a field-measured BSAF, a laboratory-measured BCF only reflects the accumulation of chemical through the water exposure route. Laboratory-measured BCFs may therefore under estimate BAFs for chemicals where accumulation from sediment or dietary sources is important. In these cases, laboratory-measured BCFs can be multiplied by a FCM to reflect accumulation from non-aqueous (i.e., food chain) pathways of exposure. Since a laboratory-measured BCF is determined using the measured concentration of a chemical in an aquatic organism and its surrounding water, a laboratory-measured BCF reflects any metabolism of the chemical that occurs in the organism, but not in the food web.

4. **K_{ow}.** A chemical's octanol-water partition coefficient, or K_{ow}, can also be used to predict a BAF for nonionic organic chemicals. This procedure is appropriate only for nonionic organic chemicals (and certain ionic organic chemicals where similar lipid and organic carbon partitioning behavior applies). The K_{ow} has been extensively correlated with the BCF for nonionic organic chemicals that are poorly metabolized by aquatic organisms. Therefore, where substantial metabolism is known to occur in biota, the K_{ow} is not used

to predict the BAF. For nonionic organic chemicals where chemical exposure through the food web is important, use of the K_{ow} alone will under predict the BAF. In such cases, the K_{ow} is adjusted with a FCM similar to the BCF procedure above.

5.3.2 Overview of BAF Derivation Framework

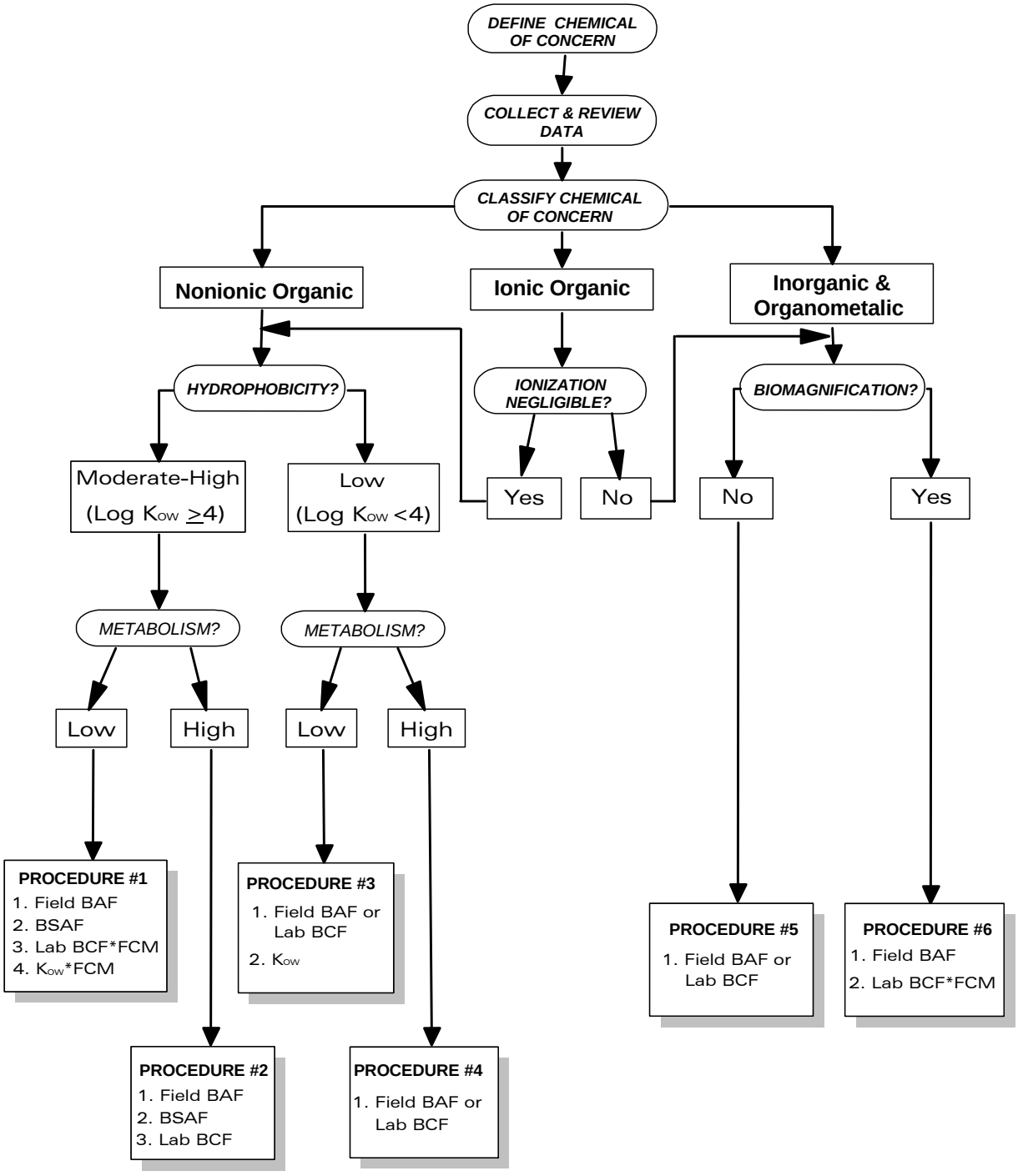
Although up to four methods can be used to derive a BAF as described in the previous section, it is evident that these methods do not apply equally to all types of chemicals. In addition, experience demonstrates that the required data will usually not be available to derive a BAF value using all of the applicable methods. As a result, EPA has developed the following guidelines to direct users in selecting the most appropriate method(s) for deriving a national BAF.

Figure 5-1 shows the overall framework of EPA's national BAF methodology. This framework illustrates the major steps and decisions that will ultimately lead to calculating a national BAF using one of six hierarchical procedures shown at the bottom of Figure 5-1. Each procedure contains a hierarchy of the BAF derivation methods discussed above, the composition of which depends on the chemical type and certain chemical properties (e.g., its degree of hydrophobicity and expected degree of metabolism and biomagnification). The number assigned to each BAF method within a procedure indicates its general order of preference for deriving a national BAF value. The goal of the framework and accompanying guidelines is to enable full use of available data and methods for deriving a national BAF value while appropriately restricting the use of certain methods to reflect their inherent limitations.

The first step in the framework is to define the chemical of concern. As described in Section 5.3.3, the chemical used to derive the national BAF should be consistent with the chemical used to derive the critical health assessment value. The second step is to collect and review all relevant data on bioconcentration and bioaccumulation of the chemical of concern (see Section 5.3.4). Once pertinent data are reviewed, the third step is to classify the chemical of concern into one of three broadly defined chemical categories: (1) nonionic organic chemicals, (2) ionic organic chemicals, and (3) and inorganic and organometallic chemicals. Guidance for classifying chemicals into these three categories is provided in Section 5.3.5.

After a chemical has been classified into one of the three categories, other information is used to select one of six hierarchical procedures to derive the national BAF. The specific procedures for deriving a BAF for each chemical group are discussed in Section 5.4 for nonionic organics, Section 5.5 for ionic organics, and Section 5.6 for inorganics and organometallics.

Figure 5-1. Framework for Deriving a National BAF



Detailed guidance concerning the first three steps of the derivation process (i.e, defining the chemical of concern, collecting and reviewing data, and classifying the chemical of concern) is provided in the following three sections.

5.3.3 Defining the Chemical of Concern

Defining the chemical of concern is the first step in deriving a national BAF. This step involves precisely defining the form(s) of the chemical upon which the national BAF value will be derived. Although this step is usually straightforward for single chemicals, complications can arise when the chemical of concern occurs as a mixture. The following guidelines should be followed for defining the chemical of concern.

1. Information for defining the chemical of concern should be obtained from the health and exposure assessment portions of the criteria derivation effort. The chemical(s) used to derive the national BAF should be consistent with the chemical(s) used to derive the reference dose (RfD), point of departure/uncertainty factor (POD/UF), or cancer potency factor.

2. In most cases, the RfD, POD/UF, or cancer potency factor will be based on a single chemical. In some cases, the RfD, POD/UF, or cancer potency factor will be based on a mixture of compounds, typically within the same chemical class (e.g., toxaphene, chlordane). In these situations, the national BAF should be derived in a manner that is consistent with the mixture used to express the health assessment.

    a. If sufficient data are available to reliably assess the bioaccumulation of each relevant compound contained in the mixture, then the national BAF(s) should be derived using the BAFs for the individual compounds of the mixture and appropriately weighted to reflect the mixture composition used to establish the RfD, POD/UF, or cancer potency factor. An example of this approach is shown in the derivation of BAFs for PCBs in the GLI Rulemaking (USEPA, 1997).

    b. If sufficient data are not available to reliably assess the bioaccumulation of individual compounds of the mixture, then the national BAF(s) should be derived using BAFs for the same or appropriately similar chemical mixture as that used to establish the RfD, POD/UF, or cancer potency value.

5.3.4 Collecting and Reviewing Data

The second step in deriving a national BAF is to collect and review all relevant bioaccumulation data for the chemical of concern. The following guidance should be followed for collecting and reviewing bioaccumulation data for deriving national BAFs.

1. All data on the occurrence and accumulation of the chemical of concern in aquatic animals and plants should be collected and reviewed for adequacy.

2. A comprehensive literature search strategy should be used for gathering bioaccumulation-related data. An example of a comprehensive literature search strategy is provided in the Bioaccumulation TSD.

3. All data that are used should contain sufficient supporting information to indicate that acceptable measurement procedures were used and that the results are probably reliable. In some cases it may be appropriate to obtain additional written information from the investigator.

4. Questionable data, whether published or unpublished, should not be used. Guidance for assessing the acceptability of bioaccumulation and bioconcentration studies is found in Sections 5.4, 5.5, and 5.6.

5.3.5 Classifying the Chemical of Concern

The next step in deriving a national BAF consists of classifying the chemical of concern into one of three categories: nonionic organic, ionic organic, and inorganic and organometallic (Figure 5-1). This step helps to determine which of the four methods described in Section 5.3.1 are appropriate for deriving BAFs. The following guidance applies for classifying the chemical of concern.

1. **Nonionic Organic Chemicals.** For the purposes of the 2000 Human Health Methodology, nonionic organic chemicals are those organic compounds that do not ionize substantially in natural bodies of water. These chemicals are also referred to as neutral or nonpolar organics in the scientific literature. Due to their neutrality, nonionic organic chemicals tend to associate with other neutral (or near neutral) compartments in aquatic ecosystems (e.g., lipid, organic carbon). Examples of nonionic organic chemicals which have been widely studied in terms of their bioaccumulation include polychlorinated biphenyls (PCBs), polychlorinated dibenzo-p-dioxins and furans, many chlorinated pesticides, and polynuclear aromatic hydrocarbons (PAHs). Procedures for deriving a national BAF for nonionic organic chemicals are provided in Section 5.4.

2. **Ionic Organic Chemicals.** For the purposes of the 2000 Human Health Methodology, ionic organic chemicals are considered to include those chemicals that contain functional groups with exchangeable protons such as hydroxyl, carboxylic, and sulfonic groups and functional groups that readily accept protons such as amino and aromatic heterocyclic nitrogen (pyridine) groups. Ionic organic chemicals undergo ionization in water, the extent of which depends on pH and the pKa of the chemical. Because the ionized species of these chemicals behave differently from the neutral species, separate guidance is provided for deriving BAFs for ionic organic chemicals. Procedures for deriving national BAFs for ionic organic chemicals are provided in Section 5.5.

3. **Inorganic and Organometallic Chemicals.** The inorganic and organometallic category is considered to include inorganic minerals, other inorganic compounds and elements, metals (e.g., copper, cadmium, chromium, zinc), metalloids (selenium, arsenic) and

organometallic compounds (e.g., methylmercury, tributyltin, tetraalkyllead). Procedures for deriving BAFs for inorganic and organometallic chemicals are provided in Section 5.6.

5.4 NATIONAL BIOACCUMULATION FACTORS FOR NONIONIC ORGANIC CHEMICALS

5.4.1 Overview

This section contains the methodology for deriving national BAFs for nonionic organic chemicals as defined in Section 5.3.5. The four general steps of this methodology are:

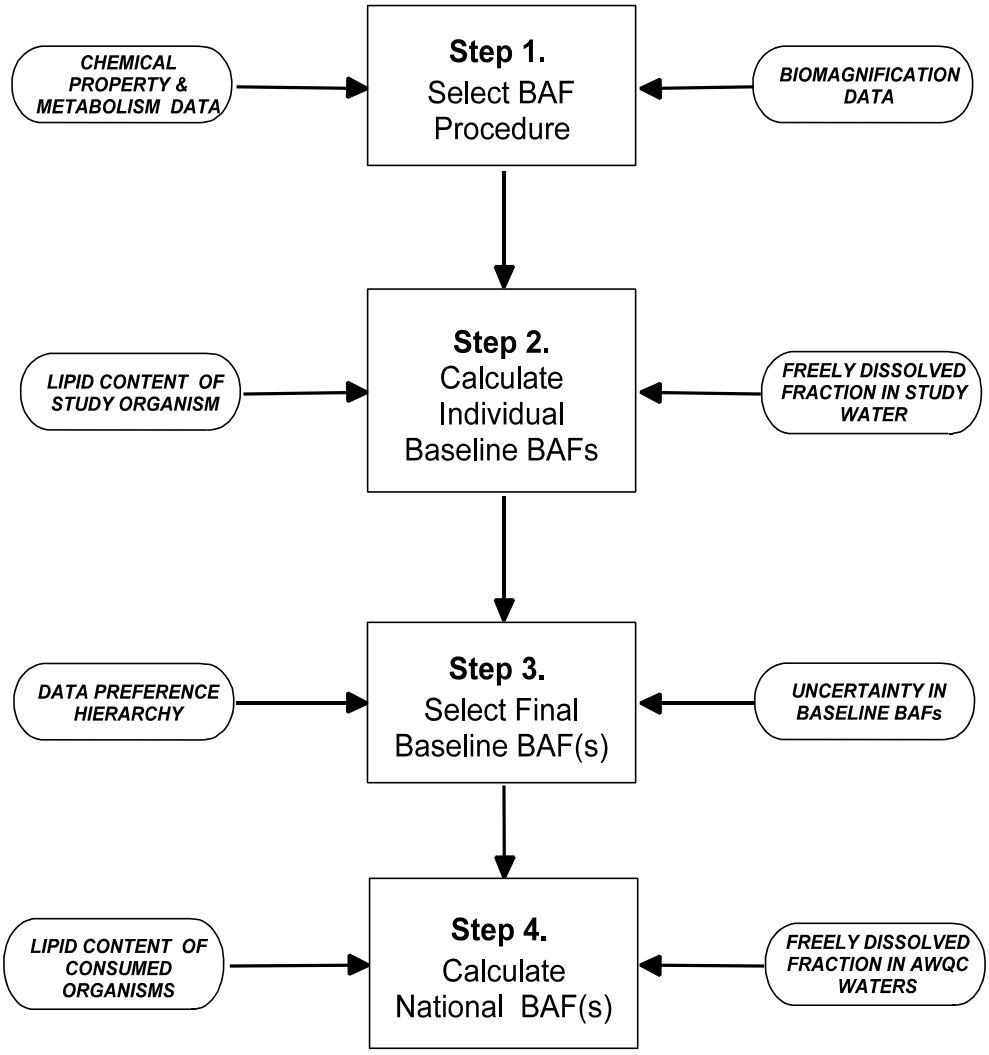
1. Selecting the BAF derivation procedure,
2. Calculating individual baseline BAF_{ℓ}^{fd}s,
3. Selecting the final baseline BAF_{ℓ}^{fd}s, and
4. Calculating the national BAFs from the final baseline BAF_{ℓ}^{fd}s.

A schematic of this four-step process is shown in Figure 5-2.

Step 1 of the methodology (selecting the BAF derivation procedure) determines which of the four BAF procedures summarized in Figure 5-1 will be appropriate for deriving the national BAF. Step 2 involves calculating individual, species-specific BAF_{ℓ}^{fd}s using all of the methods available within the selected BAF derivation procedure. Calculating the individual baseline BAF_{ℓ}^{fd}s involves using data from the field site or laboratory where the original data were collected to account for site-specific factors which affect the bioavailability of the chemical to aquatic organisms (e.g., lipid content of study organisms and freely dissolved concentration in study water). Step 3 of the methodology consists of selecting the final baseline BAF_{ℓ}^{fd}s from the individual baseline BAF_{ℓ}^{fd}s by taking into account the uncertainty in the individual BAFs and the data preference hierarchy selected in Step 1. The final step is to calculate a BAF (or BAFs) that will be used in the derivation of 304(a) criteria (i.e., referred to as the national BAF). This step involves adjusting the final baseline BAF_{ℓ}^{fd}(s) to reflect certain factors that affect bioavailablity of the chemical to aquatic organisms in waters to which the national 304(a) criteria will apply (e.g., the freely dissolved fraction expected in U.S. waters and the lipid content of consumed aquatic organisms). Baseline BAF_{ℓ}^{fd}s are not used directly in the derivation of the 304(a) criteria because they do not reflect the conditions that affect bioavailability in U.S. waters.

Section 5.4.2 below provides detailed guidance for selecting the appropriate BAF derivation procedure (Step 1 of the process). Guidance on calculating individual baseline BAF_{ℓ}^{fd}s, selecting the final baseline BAF, and calculating the national BAF (Steps 2 through 4 of the process) is provided in separate sections under each of the four BAF derivation procedures.

Figure 5-2. BAF Derivation for Nonionic Organic Chemicals



5.4.2 Selecting the BAF Derivation Procedure

This section describes the decisions that should be made to select one of the four available hierarchical procedures for deriving a national BAF for nonionic organic chemicals (Procedures #1 through #4 of Figure 5-1). As shown in Figure 5-1, two decision points exist in selecting the BAF derivation procedure. The first decision point requires knowledge of the chemical's hydrophobicity (i.e., the K_{ow} of the chemical). Guidance for selecting the K_{ow} for a chemical is provided in the Bioaccumulation TSD. The K_{ow} provides an initial basis for assessing whether biomagnification may be a concern for nonionic organic chemicals. The second decision point is based on the rate of metabolism for the chemical in the target organism. Guidance for assessing whether a high or low rate of metabolism is likely for a chemical of concern is provided below in Section 5.4.2.3. With the appropriate information for these two decision points, the BAF derivation procedure should be selected using the following guidelines.

5.4.2.1 <u>Chemicals with Moderate to High Hydrophobicity</u>

1. For the purposes of the 2000 Human Health Methodology, nonionic organic chemicals with log K_{ow} values equal to or greater than 4.0 should be classified as moderately to highly hydrophobic. For moderately to highly hydrophobic nonionic organic chemicals, available data indicate that exposure through the diet and other non-aqueous routes can become important in determining chemical residues in aquatic organisms (e.g., Russell et al., 1999; Fisk et al., 1998; Oliver and Niimi, 1983; Oliver and Niimi, 1988; Niimi, 1985; Swackhammer and Hites, 1988). Dietary and other non-aqueous exposure can become extremely important for those nonionic organic chemicals that are poorly metabolized by aquatic biota (e.g., certain PCB congeners, chlorinated pesticides, and polychlorinated dibenzo-p-dioxins and furans).

2. **Procedure #1** should be used to derive national BAFs for moderately to highly hydrophobic nonionic organic chemicals in cases where:

   (a) the rate of chemical metabolism by target aquatic organisms is expected to be sufficiently low such that biomagnification is of concern, or

   (b) the rate of chemical metabolism by target aquatic organisms is not sufficiently known.

   Procedure #1 accounts for non-aqueous exposure and the potential for biomagnification in aquatic food webs through the use of field-measured values for bioaccumulation (i.e., field measured BAF or BSAF) and FCMs when appropriate field data are unavailable. Guidance on deriving national BAFs using Procedure #1 is found below in Section 5.4.3.

3. **Procedure #2** should be used to derive the national BAFs for moderately to highly hydrophobic nonionic organic chemicals in cases where:

   (a) the rate of chemical metabolism by target aquatic organisms is expected to be sufficiently high such that biomagnification is not of concern.

Procedure #2 relaxes the requirement of using FCMs and eliminates the use of K_{ow}-based estimates of the BAF, two procedures that are most appropriate for poorly metabolized nonionic organic chemicals. Guidance on deriving national BAFs using Procedure #2 is found below in Section 5.4.4.

5.4.2.2 Chemicals with Low Hydrophobicity

1. For the purposes of these guidelines, nonionic organic chemicals with log K_{ow} values less than 4.0 should be classified as exhibiting low hydrophobicity. For nonionic organic chemicals that exhibit low hydrophobicity (i.e., log $K_{ow} < 4.0$), available information indicates that non-aqueous exposure to these chemicals is not likely to be important in determining chemical residues in aquatic organisms (e.g., Fisk et al., 1998; Gobas et al., 1993; Connolly and Pedersen, 1988; Thomann, 1989). For this group of chemicals, laboratory-measured BCFs and K_{ow}-predicted BCFs do not require adjustment with FCMs for determining the national BAF (Procedures #3 and #4), unless other appropriate data indicate differently.

   Other appropriate data include studies clearly indicating that non-aqueous exposure is important such that use of a BCF would substantially underestimate residues in aquatic organisms. In these cases, Procedure #1 should be used to derive the BAF for nonionic organic chemicals with log $K_{ow} < 4.0$. Furthermore, the data supporting the K_{ow} determination should be carefully reviewed for accuracy and appropriate interpretation, since the apparent discrepancy may be due to errors in determining K_{ow}.

2. **Procedure #3** should be used to derive national BAFs for nonionic organic chemicals of low hydrophobicity in cases where:

   (a) the rate of chemical metabolism by target aquatic organisms is expected to be negligible, such that tissue residues of the chemical of concern are not substantially reduced compared to an assumption of no metabolism, or

   (b) the rate of chemical metabolism by target aquatic organisms is not sufficiently known.

   Procedure #3 includes the use of K_{ow}-based estimates of the BCF to be used when lab or field data are absent. Guidance on deriving national BAFs using Procedure #3 is found below in Section 5.4.5.

3. **Procedure #4** should be used to derive national BAFs for nonionic organic chemicals of low hydrophobicity in cases where:

   (a) the rate of chemical metabolism by target aquatic organisms is expected to be sufficiently high, such that tissue residues of the chemical of concern are substantially reduced compared with an assumption of no metabolism.

Procedure #4 eliminates the option of using K_{ow}-based estimates of the BAF because the K_{ow} may over-predict accumulation when a chemical is metabolized substantially by an aquatic organism. Guidance on deriving national BAFs using Procedure #4 is found below in Section 5.4.6.

5.4.2.3 Assessing Metabolism

Currently, assessing the degree to which a chemical is metabolized by aquatic organisms is confounded by a variety of factors. First, conclusive data on chemical metabolism in aquatic biota are largely lacking. Such data include whole organism studies where the metabolic rates and breakdown products are quantified in fish and other aquatic organisms relevant to human consumption. However, the majority of information on metabolism is derived from *in vitro* liver microsomal preparations in which primary and secondary metabolites may be identified and their rates of formation may or may not be quantified. Extrapolating results from *in vitro* studies to the whole organism involves considerable uncertainty. Second, there are no generally accepted procedures for reliably predicting chemical metabolism by aquatic organisms in the absence of measured data. Third, the rate at which a chemical is metabolized by aquatic organisms can be species and temperature dependent. For example, PAHs are known to be metabolized readily by vertebrate aquatic species (primarily fish), although at rates much less than those observed for mammals. However, the degree of metabolism in invertebrate species is generally much less than the degree in vertebrate species (James, 1989). One hypothesis for this difference is that the invertebrate species lack the detoxifying enzymes and pathways that are present in many vertebrate species.

Given the current limitations on assessing the degree of chemical metabolism by aquatic organisms, the assessment of metabolism should be made on a case-by-case basis using a weight-of-evidence approach. When assessing a chemical's likelihood to undergo substantial metabolism in a target aquatic organism, the following data should be carefully evaluated:

(1) *in vivo* chemical metabolism data,
(2) bioconcentration and bioaccumulation data,
(3) data on chemical occurrence in target aquatic biota, and
(4) *in vitro* chemical metabolism data.

1. ***In vivo* Data.** *In vivo* data on metabolism in aquatic organisms are from studies of chemical metabolism using whole organisms. These studies are usually conducted using large fish from which blood, bile, urine, and individual tissues can be collected for the identification and quantification of metabolites formed over time. *In vivo* studies are considered the most useful for evaluating a chemical's degree of metabolism in an organism because both oxidative (Phase I) and conjugative (Phase II) metabolism can be assessed in these studies. Mass-balance studies, in which parent compound elimination is quantified separately from biotransformation and elimination of metabolites, allow calculation of conversion rate of parent to metabolite as well as metabolite elimination. This information might be used to estimate loss due to metabolism separately from that due to elimination of the parent compound for adjustment of K_{ow}-predicted BAFs. However, due to the analytical and experimental challenges these studies pose, data of

this type are limited. Less rigorous *in vivo* metabolism studies might include the use of metabolic blockers to demonstrate the influence of metabolism on parent compound kinetics. However, caution should be used in interpretation of absolute rates from these data due to the lack of specificity of mammalian derived blockers in aquatic species (Miranda et al., 1998).

2. **Bioconcentration or Bioaccumulation Data.** Data on chemical bioconcentration or bioaccumulation in aquatic organisms can be used indirectly for assessing metabolism. This assessment involves comparing acceptable lab-measured BCFs or field-measured BAFs (after converting to baseline values using procedures below) with the chemical's predicted value based on K_{ow}. The theoretical basis of bioconcentration and bioaccumulation for nonionic organic chemicals indicates that a chemical's baseline BCF should be similar to its K_{ow}-predicted value if metabolism is not occurring or is minimal (see the Bioaccumulation TSD). This theory also indicates that baseline BAFs should be similar to or higher than the K_{ow} for poorly metabolized organic chemicals, with highly hydrophobic chemicals often exhibiting higher baseline BAFs than K_{ow} values. Thus, if a chemical's baseline BCF or BAF is substantially lower than its K_{ow}, this may be an indication that the chemical is being metabolized by the aquatic organism of concern. Note, however, that this difference may also indicate problems in the experimental design or analytical chemistry, and that it may be difficult to discern the difference.

3. **Chemical Occurrence Data.** Although by no means definitive, data on the occurrence of chemicals in aquatic biota (i.e., residue studies) may offer another useful line of evidence for evaluating a chemical's likelihood to undergo substantial metabolism. Such studies are most useful if they have been conducted repeatedly over time and over wide geographical areas. Such studies might indicate a chemical is poorly metabolized if data show that the chemical is being biomagnified in the aquatic food web (i.e., higher lipid-normalized residues in successive trophic levels). Conversely, such studies might indicate a chemical is being metabolized substantially if residue data show a decline in residues with increasing trophic level. Again, other reasons for increases or decreases in concentrations with increasing trophic level might exist and should be carefully evaluated (e.g., incorrect food web assumptions, differences in exposure concentrations).

4. ***In vitro* Data.** *In vitro* metabolism data include data from studies where specific sub-cellular fractions (e.g., microsomal, cytosolic), cells, or tissues from an organism are tested outside the body (i.e., in test-tubes, cell- or tissue-culture). Compared with *in vivo* studies of chemical metabolism in aquatic organisms, *in vitro* studies are much more plentiful in the literature, with the majority of studies characterizing oxidative (Phase I) reactions de-coupled from conjugative (Phase II) metabolism. Cell, tissue, or organ level *in vitro* studies are less common but provide a more complete assessment of metabolism. While such studies are particularly useful for identifying the pathways, rates of formation, and metabolites formed, as well as the enzymes involved and differences in the temperature dependence of metabolism across aquatic species, they suffer from uncertainty when results are extrapolated to the whole organism. This uncertainty results from the fact that dosimetry (i.e., delivery of the toxicant to, and removal of metabolite

from, the target tissue) cannot currently be adequately reproduced in the laboratory or easily modeled.

When assessing chemical metabolism using the above information, the following guidelines apply.

a. A finding of substantial metabolism should be supported by two or more lines of evidence identified using the data described above.

b. At least one of the lines of evidence should be supported by either *in vivo* metabolism data or acceptable bioconcentration or bioaccumulation data.

c. A finding of substantial metabolism in one organism should not be extrapolated to another organism or another group of organisms unless data indicate similar metabolic pathways exist (or are very likely to exist) in both organisms. *In vitro* data may be particularly useful in cross-species extrapolations.

d. Finally, in situations where sufficient data are not available to properly assess the likelihood of significant metabolism in aquatic biota of concern, the chemical should be assumed to undergo little or no metabolism. This assumptions reflects a policy decision by EPA to err on the side of public health protection when sufficient information on metabolism is lacking.

5.4.3 Deriving National BAFs Using Procedure #1

This section contains guidance for calculating national BAFs for nonionic organic chemicals using Procedure #1 shown in Figure 5-1. The types of nonionic organic chemicals for which Procedure #1 is most appropriate are those that are classified as moderately to highly hydrophobic and subject to low (or unknown) rates of metabolism by aquatic biota (see Section 5.4.2 above). Non-aqueous contaminant exposure and subsequent biomagnification in aquatic food webs are of concern for chemicals that are classified in this category. Some examples of nonionic organic chemicals for which Procedure #1 is considered appropriate include:

- tetra-, penta- & hexachlorobenzenes;
- PCBs;
- octachlorostyrene;
- hexachlorobutadiene;
- endrin, dieldrin, aldrin;
- mirex, photomirex;
- DDT, DDE, DDD; and
- heptachlor, chlordane, nonachlor.

Under Procedure #1, the following four methods may be used in deriving a national BAF:

- using a BAF from an acceptable field study (i.e., a field-measured BAF);
- predicting a BAF from an acceptable field-measured BSAF;

- predicting a BAF from an acceptable laboratory-measured BCF and FCM; and
- predicting a BAF from an acceptable K_{ow} and FCM.

As shown in Figure 5-2, once the derivation procedure has been selected, the next steps in deriving a national BAF for a given trophic level include: calculating individual baseline BAF_{ℓ}^{fd}s (step 2), selecting the final baseline BAF_{ℓ}^{fd} (step 3), and calculating the national BAF from the final baseline BAF_{ℓ}^{fd} (step 4). Each of these three steps is discussed separately below.

5.4.3.1 Calculating Individual Baseline BAF_{ℓ}^{fd}s

Calculating an individual baseline BAF_{ℓ}^{fd} involves normalizing the field-measured BAF_{T}^{t} (or laboratory-measured BCF_{T}^{t}) which are based on total concentrations in tissue and water by the lipid content of the study organisms and the freely dissolved concentration in the study water. Both the lipid content in the organism and the freely dissolved concentration (as influenced by organic carbon in water) have been shown to be important factors that influence the bioaccumulation of nonionic organic chemicals (e.g., Mackay, 1982; Connolly and Pederson, 1988; Thomann, 1989, Suffet et al., 1994). Therefore, baseline BAF_{ℓ}^{fd}s (which are expressed on a freely dissolved and lipid-normalized basis) are considered more amenable to extrapolating between different species and bodies of water compared to BAFs expressed using the total concentration in the tissue and water. Because bioaccumulation can be strongly influenced by the trophic position of aquatic organisms (either due to biomagnification or physiological differences), extrapolation of baseline BAF_{ℓ}^{fd}s should not be performed between species of different trophic levels.

1. For each species for which acceptable data are available, calculate all possible baseline BAF_{ℓ}^{fd}s using each of the four methods shown above for Procedure #1.

2. Individual baseline BAF_{ℓ}^{fd}s should be calculated from field-measured BAF_{T}^{t}s, field-measured BSAFs, laboratory BCF_{T}^{t}s, and the K_{ow} according to the following procedures.

A. Baseline BAF_{ℓ}^{fd}s from Field-Measured BAFs

A baseline BAF_{ℓ}^{fd} should be calculated from each field-measured BAF_{T}^{t} using information on the lipid fraction in the tissue of concern for the study organism and the fraction of the total chemical that is freely dissolved in the study water.

1. **Baseline BAF_{ℓ}^{fd} Equation.** For each acceptable field-measured BAF_{T}^{t}, calculate a baseline BAF_{ℓ}^{fd} using the following equation:

$$\text{Baseline } BAF_{\ell}^{fd} = \left[\frac{\text{Measured } BAF_{T}^{t}}{f_{fd}} - 1 \right] \left(\frac{1}{f_{\ell}} \right) \qquad \text{(Equation 5-10)}$$

where:

Baseline BAF_{ℓ}^{fd}	=	BAF expressed on a freely dissolved and lipid-normalized basis
Measured BAF_{T}^{t}	=	BAF based on total concentration in tissue and water
f_{ℓ}	=	Fraction of the tissue that is lipid
f_{fd}	=	Fraction of the total chemical that is freely dissolved in the ambient water

The technical basis of Equation 5-10 is provided in the Bioaccumulation TSD. Guidance for determining each component of Equation 5-10 is provided below.

2. **Determining the Measured BAF_{T}^{t}.** The field-measured BAF_{T}^{t} shown in Equation 5-10 should be calculated based on the total concentration of the chemical in the appropriate tissue of the aquatic organism and the total concentration of the chemical in ambient water at the site of sampling. The equation to derive a measured BAF_{T}^{t} is:

$$\text{Measured } BAF_{T}^{t} = \frac{C_t}{C_w} \qquad \text{(Equation 5-11)}$$

where:

C_t	=	Total concentration of the chemical in the specified wet tissue
C_w	=	Total concentration of chemical in water

The data used to calculate a field-measured BAF_{T}^{t} should be reviewed thoroughly to assess the quality of the data and the overall uncertainty in the BAF value. The following general criteria apply in determining the acceptability of field-measured BAFs that are being considered for deriving national BAFs using Procedure #1.

a. Aquatic organisms used to calculate a field-measured BAF_{T}^{t} should be representative of aquatic organisms that are commonly consumed in the United States. An aquatic organism that is not commonly consumed in the United States can be used to calculate an acceptable field-measured BAF_{T}^{t} provided that the organism is considered to be a reasonable surrogate for a commonly consumed organism. Information on the ecology, physiology, and biology of the organism should be reviewed when assessing whether an organism is a reasonable surrogate of a commonly consumed organism.

b. The trophic level of the study organism should be determined by taking into account its life stage, diet, size, and the food web structure at the study location. Information from the study site (or similar sites) is preferred when evaluating trophic status. If such information is lacking, general information for assessing trophic status of aquatic organisms can be found in USEPA (2000a,b,c).

c. The percent lipid of the tissue used to determine the field-measured BAF_T^t should be either measured or reliably estimated to permit lipid-normalization of the chemical's tissue concentration.

d. The study from which the field-measured BAF_T^t is derived should contain sufficient supporting information from which to determine that tissue and water samples were collected and analyzed using appropriate, sensitive, accurate, and precise analytical methods.

e. The site of the field study should not be so unique that the BAF cannot be reasonably extrapolated to other locations where the BAF and resulting criteria will apply.

f. The water concentration(s) used to derive the BAF should reflect the average exposure of the aquatic organism that corresponds to the concentration measured in its tissue of concern. For nonionic organic chemicals, greater temporal and spatial averaging of chemical concentrations is required as the K_{ow} increases. In addition, as variability in water concentrations increase, greater temporal and spatial averaging is also generally required. Greater spatial averaging is also generally required for more mobile organisms.

g. The concentrations of particulate organic carbon and dissolved organic carbon in the study water should be measured or reliably estimated.

EPA is currently developing guidance for designing and conducting field studies for determining field-measured BAF_T^ts, including recommendations for minimum data requirements. A more detailed discussion of factors that should be considered when determining field-measured BAF_T^ts is provided in the Bioaccumulation TSD.

3. **Determining the Fraction Freely Dissolved (f_{fd}).** As illustrated by Equation 5-10, the fraction of the nonionic organic chemical that is freely dissolved in the study water is required for calculating a baseline BAF_ℓ^{fd} from a field-measured BAF_T^t. The freely dissolved fraction is the portion of the nonionic organic chemical that is not bound to particulate organic carbon or dissolved organic carbon. Together, the concentration of a nonionic organic chemical that is freely dissolved, bound to dissolved organic carbon, and bound to particulate organic carbon constitute its total concentration in water. As discussed further in the Bioaccumulation TSD, the freely dissolved fraction of a chemical is considered to be the best expression of the bioavailable form of nonionic organic chemicals to aquatic organisms (e.g., Suffet et al., 1994; USEPA, 1995b). Because the fraction of a nonionic organic chemical that is freely dissolved may vary among different bodies of water as a result of differences in dissolved and particulate organic carbon in the water, the bioavailability of the total chemical concentration in water is expected to vary from one body of water to another. Therefore, BAFs which are based on the freely dissolved concentration in water (rather than the total concentration in water) are considered to be more reliable for extrapolating and aggregating BAFs among different bodies of water. Currently, availability of BAFs based on measured freely dissolved

concentrations is very limited, partly because of difficulties in analytically measuring the freely dissolved concentration. Thus, if a BAF based on the total water concentration is reported in a given study, the fraction of the chemical that is freely dissolved should be predicted using information on the organic carbon content in the study water.

a. **Equation for Determining the Freely Dissolved Fraction.** If reliable measured data are unavailable to directly determine the freely dissolved fraction of the chemical in water, the freely dissolved fraction should be estimated using the following equation.

$$f_{fd} = \frac{1}{[1 + (POC \cdot K_{ow}) + (DOC \cdot 0.08 \cdot K_{ow})]} \qquad \text{(Equation 5-12)}$$

where:

POC	=	concentration of particulate organic carbon (kg/L)
DOC	=	concentration of dissolved organic carbon (kg/L)
K_{ow}	=	n-octanol water partition coefficient for the chemical

In Equation 5-12, K_{ow} is being used to estimate the partition coefficient to POC (i.e., K_{POC} in L/kg) and $0.08 \cdot K_{ow}$ is being used to estimate the partition coefficient to DOC (i.e., the K_{DOC} in L/kg). A discussion of the technical basis, assumptions, and uncertainty associated with the derivation and application of Equation 5-12 is provided in the Bioaccumulation TSD.

b. **POC and DOC Values.** When converting from the total concentration of a chemical to a freely dissolved concentration using Equation 5-12 above, the POC and DOC concentrations should be obtained from the original study from which the field-measured BAF is determined. If POC and DOC concentrations are not reported in the BAF study, reliable estimates of POC and DOC might be obtained from other studies of the same site used in the BAF study or closely related site(s) within the same water body. When using POC/DOC data from other studies of the same water body, care should be taken to ensure that environmental and hydrological conditions that might affect POC or DOC concentrations (i.e., runoff events, proximity to ground water or surface water inputs, sampling season) are reasonably similar to those in the BAF study. Additional information related to selecting POC and DOC values is provided in the Bioaccumulation TSD.

In some cases, BAFs are reported using the concentration of the chemical in filtered or centrifuged water. When converting these BAFs to a freely dissolved basis, the concentration of POC should be set equal to zero when using Equation 5-12. Particulates are removed from water samples by filtering or centrifuging the sample.

c. **Selecting K_{ow} Values.** A variety of techniques are available to measure or predict K_{ow} values. The reliability of these techniques depends to a large extent on the K_{ow} of the chemical. Because K_{ow} is an important input parameter for calculating the freely dissolved concentration of nonionic organic chemicals and for deriving BAFs using the other three methods of Procedure #1, care should be taken in selecting the most reliable K_{ow} value. The value of K_{ow} for use in estimating the freely dissolved fraction and other procedures used to derive national BAFs should be selected based on the guidance presented in the Bioaccumulation TSD.

4. **Determining the Fraction Lipid (f_ℓ).** Calculating a baseline BAF_ℓ^{fd} for a nonionic organic chemical using Equation 5-10 also requires that the total chemical concentration measured in the tissue used to determine the field-measured BAF_T^t be normalized by the lipid fraction (f_ℓ) in that same tissue. Lipid normalization of tissue concentrations reflects the assumption that BAFs (and BCFs) for nonionic organic chemicals are directly proportional to the percent lipid in the tissue upon which they are based. This assumption means that an organism with a two percent lipid content would be expected to accumulate twice the amount of a chemical at steady state compared with an organism with one percent lipid content, all else being equal. The assumption that aquatic organisms accumulate nonionic organic chemicals in proportion to their lipid content has been extensively evaluated in the literature (Mackay, 1982; Connell, 1988; Barron, 1990) and is generally accepted. Because the lipid content in aquatic organisms can vary both within and across species, BAFs that are expressed using the lipid-normalized concentration (rather than the total concentration in tissue) are considered to be the most reliable for aggregating multiple BAF values for a given species. Additional discussion of technical basis, assumptions, and uncertainties involved in lipid normalization is provided in the Bioaccumulation TSD.

a. The lipid fraction f_ℓ, is routinely reported in bioaccumulation studies involving nonionic organic chemicals. If the lipid fraction is not reported in the BAF study, it can be calculated using the following equation if the appropriate data are reported:

$$f_\ell = \frac{M_\ell}{M_t} \qquad \text{(Equation 5-13)}$$

where:

M_ℓ = Mass of lipid in specified tissue
M_t = Mass of specified tissue (wet weight)

b. Because lipid content can vary within an aquatic organism (and among tissues within that organism) due to several factors including the age and sex of the organism, changes in dietary composition, season of sampling and reproductive status, the lipid fraction used to calculate a baseline BAF_ℓ^{fd} should be measured in

the same tissue and organisms used to determine the field-measured BAF_T^t, unless comparability is demonstrated across organisms.

c. Experience has shown that different solvent systems used to extract lipids for analytical measurement can result in different quantities of lipids being extracted and measured in aquatic organisms (e.g., Randall et al.,1991, 1998). As a result, lipid measurements determined using different solvent systems might lead to apparent differences in lipid-normalized concentrations and lipid-normalized BAFs. The extent to which different solvent systems might affect lipid extractions (and lipid-normalized concentrations) is thought to vary depending on the solvent, chemical of concern, and lipid composition of the tissue being extracted. Guidance on measurement of lipid content, including the choice of solvent system and how different solvent systems may affect lipid content, is provided in the Bioaccumulation TSD.

B. Baseline BAF_ℓ^{fd} Derived from BSAFs

The second method of determining a baseline BAF_ℓ^{fd} for the chemical of concern in Procedure #1 involves the use of BSAFs. Although BSAFs may be used for measuring and predicting bioaccumulation directly from concentrations of chemicals in surface sediment, they may also be used to estimate BAFs (USEPA, 1995b; Cook and Burkhard, 1998). Since BSAFs are based on field data and incorporate effects of chemical bioavailability, food web structure, metabolism, biomagnification, growth, and other factors, BAFs estimated from BSAFs will incorporate the net effect of all these factors. The BSAF approach is particularly beneficial for developing water quality criteria for chemicals which are detectable in fish tissues and sediments, but are difficult to detect or measure precisely in the water column.

As shown by Equation 5-14 below, predicting baseline BAF_ℓ^{fd}s using BSAFs requires that certain types of data be used for the chemicals of interest (for which BAFs are to be determined) and reference chemicals (for which BAFs are measured) from a common sediment-water-organism data set. Differences between BSAFs for different organic chemicals are good measures of the relative bioaccumulation potentials of the chemicals. When calculated from a common organism-sediment sample set, chemical-specific differences in BSAFs reflect the net effect of biomagnification, metabolism, food chain, bioenergetics, and bioavailability factors on the degree of each chemical's equilibrium/disequilibrium between sediment and biota. At equilibrium, BSAFs are expected to be approximately 1.0. However, deviations from 1.0 (reflecting disequilibrium) are common due to: conditions where water is not at equilibrium with surface sediment; differences in organic carbon content of water and sediment; kinetic limitations for chemical transfer between sediments and water associated with specific biota; biomagnification; or biological processes such as growth or biotransformation. BSAFs are most useful (i.e., most predictable from one site to another) when measured under steady-state (or near steady-state) conditions. The use of non-steady-state BSAFs, such as found with new chemical loadings or rapid increases in loadings, increases uncertainty in this method for the relative degree of disequilibrium between the reference chemicals and the chemicals of interest. In general, the fact that concentrations of hydrophobic chemicals in sediment are less sensitive than concentrations in water to fluctuations in chemical loading and distribution makes the BSAF

method robust for estimating BAFs. Results from validation of the BAF procedure in Lake Ontario, the Fox River and Green Bay, Wisconsin, and the Hudson River, New York, demonstrate good agreement between observed and BSAF-predicted BAFs in the vast majority of comparisons made. Detailed results of the validation studies for the BSAF procedure are provided in the Bioaccumulation TSD.

Baseline BAF_{ℓ}^{fd}s should be calculated using acceptable BSAFs for chemicals of interest and appropriate sediment-to-water fugacity (disequilibrium) ratios $(\prod_{socw})_r/(K_{ow})_r$ for reference chemicals under the following guidelines.

1. **Baseline BAF_{ℓ}^{fd} Equation.** For each species with an acceptable field measured $(BSAF)_I$, a baseline BAF_{ℓ}^{fd} for the chemical of interest may be calculated using the following equation with an appropriate value of $(\prod_{socw})_r/(K_{ow})_r$:

$$(Baseline\ BAF_{\ell}^{fd})_i = (BSAF)_i \frac{(D_{i/r})\ (\prod_{socw})_r\ (K_{ow})_i}{(K_{ow})_r} \qquad \text{(Equation 5-14)}$$

where:

$(\text{Baseline } BAF_{\ell}^{fd})_I$	=	BAF expressed on a freely dissolved and lipid-normalized basis for chemical of interest "I"
$(BSAF)_I$	=	Biota-sediment accumulation factor for chemical of interest "I"
$(\prod_{socw})_r$	=	sediment organic carbon to water freely dissolved concentration ratio of reference chemical "r"
$(K_{ow})_I$	=	octanol-water partition coefficient for chemical of interest "I"
$(K_{ow})_r$	=	octanol-water partition coefficient for the reference chemical "r"
$D_{i/r}$	=	ratio between $\prod_{socw}/K_{ow}$ for chemicals "I" and "r" (normally chosen so that $D_{i/r} = 1$)

The technical basis, assumptions, and uncertainties associated with Equation 5-14 are provided in the Bioaccumulation TSD. Guidance for determining each component of Equation 5-14 is provided below.

2. **Determining Field-Measured BSAFs.** BSAFs should be determined by relating lipid-normalized concentrations of chemicals in an organism (C_{ℓ}) to organic carbon-normalized concentrations of the chemicals in surface sediment samples (C_{soc}) using the following equation:

$$BSAF = \frac{C_{\ell}}{C_{soc}} \qquad \text{(Equation 5-15)}$$

a. **Lipid-Normalized Concentration.** The lipid-normalized concentration of a chemical in an organism should be determined by:

$$C_{\ell} = \frac{C_t}{f_{\ell}} \qquad \text{(Equation 5-16)}$$

where:

C_t = Concentration of the chemical in the wet tissue (either whole organism or specified tissue) (µg/g)
f_{ℓ} = Fraction lipid content in the tissue

b. **Organic Carbon-Normalized Concentration.** The organic carbon-normalized concentration of a chemical in sediment should be determined by:

$$C_{soc} = \frac{C_s}{f_{oc}} \qquad \text{(Equation 5-17)}$$

where:

C_s = Concentration of chemical in sediment (µg/g sediment)
f_{oc} = Fraction organic carbon in sediment

The organic carbon-normalized concentrations of the chemicals in surface sediment samples should be associated with the average exposure environment of the organism.

3. **Sediment-to-Water Partition Coefficient** $(\prod_{socw})_r$. Sediment-to-water partition coefficients for reference chemicals should be determined by:

$$(\prod_{socw})_r = \frac{(C_{soc})_r}{(C_w^{fd})_r} \qquad \text{(Equation 5-18)}$$

where:

$(C_{soc})_r$ = Concentration of a reference chemical in sediment normalized to sediment organic carbon
$(C_w^{fd})_r$ = Concentration of the reference chemical freely dissolved in water

4. **Selecting Reference Chemicals.** Reference chemicals with $(\prod_{socw}) / (K_{ow})$ similar to that of the chemical of interest are preferred for this method. Theoretically, knowledge of the

difference between sediment-to-water fugacity ratios for two chemicals, "I" and "r" ($D_{i/r}$), could be used when reliable reference chemicals that meet the fugacity equivalence condition are not available. Similarity of $(\prod_{socw}) / (K_{ow})$ for two chemicals can be indicated on the basis of similar physical-chemical behavior in water (persistence, volatilization), similar mass loading histories, and similar concentration profiles in sediment cores.

Validation studies have demonstrated that choosing reference chemicals with well quantified concentrations in water is important because the uncertainty associated with measurement of barely detected chemicals is large (see the Bioaccumulation TSD). Similarity between K_{ow} values of the reference and target chemicals is generally desirable, although recent validation studies indicate that the accuracy of the method is not substantially decreased through use of reference chemicals with large differences in K_{ow}, as long as the chemicals are structurally similar and have similar persistence behavior in water and sediments.

5. The following data, procedural, and quality assurance requirements should be met for predicting baseline BAF_{ℓ}^{fd}s using field-measured BSAFs:

   a. Data on the reference chemicals and chemicals of interest should come from a common organism-water-sediment data set at a particular site.

   b. The chemicals of interest and reference chemicals should have similar physicochemical properties and persistence in water and sediment.

   c. The loadings history of the reference chemicals and chemicals of interest should be similar such that their expected sediment-water disequilibrium ratios $(\prod_{socw}/K_{ow})$ would not be expected to be substantially different (i.e., $D_{i/r} \sim 1$).

   d. The use of multiple reference chemicals is generally preferred for determining the value of $(\prod_{socw})_r$ so long as the concentrations are well quantified and the aforementioned conditions for selecting reference chemicals are met. In some cases, use of a single reference chemical may be necessary because of limited data.

   e. Samples of surface sediments (0-1 cm is ideal) should be from locations in which sediment is regularly deposited and is representative of average surface sediment in the vicinity of the organism.

   f. The K_{ow} value for the target and reference chemicals should be selected as described in the Bioaccumulation TSD.

   g. All other data quality and procedural guidelines described earlier for determining field-measured BAFs in Section 5.4.3.1(A) should be met.

Further details on the requirements for predicting BAFs from BSAF measurements, including the data, assumptions, and limitations of this approach are provided in the Bioaccumulation TSD.

C. Baseline BAF_{ℓ}^{fd} from a Laboratory-Measured BCF_T^t and FCM

The third method in Procedure #1 consists of using a laboratory-measured BCF_T^t (i.e., a BCF based on total concentrations in tissue and water) and FCMs to predict a baseline BAF_{ℓ}^{fd} for the chemical of concern. The BCF_T^t is used in conjunction with an FCM because non-aqueous routes of exposure and subsequent biomagnification is of concern for the types of chemicals applicable to Procedure #1. A laboratory-measured BCF inherently accounts for the effects of chemical metabolism that occurs in the organism used to calculate the BCF, but does not account for metabolism which may occur in other organisms of the aquatic food web.

1. **Baseline BAF_{ℓ}^{fd} Equation.** For each acceptable laboratory-measured BCF_T^t, calculate a baseline BAF_{ℓ}^{fd} using the following equation:

$$\text{Baseline } BAF_{\ell}^{fd} = (FCM) \cdot \left[\frac{\text{Measured } BCF_T^t}{f_{fd}} - 1 \right] \cdot \left(\frac{1}{f_{\ell}} \right) \qquad \text{(Equation 5-19)}$$

where:

Baseline BAF_{ℓ}^{fd}	=	BAF expressed on a freely dissolved and lipid-normalized basis
Measured BCF_T^t	=	BCF based on total concentration in tissue and water
f_{ℓ}	=	Fraction of the tissue that is lipid
f_{fd}	=	Fraction of the total chemical in the test water that is freely dissolved
FCM	=	The food chain multiplier either obtained from Table 5-1 by linear interpolation for the appropriate trophic level, or from appropriate field data

The technical basis for Equation 5-19 is provided in the Bioaccumulation TSD. Guidance for determining each component of Equation 5-19 is provided below.

2. **Determining the Measured BCF_T^t.** The laboratory-measured BCF_T^t shown in Equation 5-19 should be calculated using information on the total concentration of the chemical in the tissue of the organism and the total concentration of the chemical in the laboratory test water. The equation to derive a measured BCF_T^t is:

$$\text{Measured } BCF_T^t = \frac{C_t}{C_w} \qquad \text{(Equation 5-20)}$$

where:

C_t = Total concentration of the chemical in the specified wet tissue
C_w = Total concentration of chemical in the laboratory test water

The data used to calculate a laboratory-measured BCF_T^t should be reviewed thoroughly to assess the quality of the data and the overall uncertainty in the BCF value. The following general criteria apply in determining the acceptability of laboratory-measured BCF_T^t.

a. The test organism should not be diseased, unhealthy, or adversely affected by the concentration of the chemical because these attributes may alter accumulation of chemicals compared with healthy organisms.

b. The total concentration of the chemical in the water should be measured and should be relatively constant during the exposure period.

c. The organisms should be exposed to the chemical using a flow-through or renewal procedure.

d. The percent lipid of the tissue used to normalize the BCF_T^t should be either measured or reliably estimated to permit lipid normalization of chemical concentrations.

e. The concentrations of particulate organic carbon and dissolved organic carbon in the study water should be measured or reliably estimated.

f. Aquatic organisms used to calculate a laboratory-measured BCF_T^t should be representative of those aquatic organisms that are commonly consumed in the United States. An aquatic organism which is not commonly consumed in the United States can be used to calculate an acceptable laboratory-measured BCF_T^t provided that the organism is considered to be a reasonable surrogate for a commonly consumed organism. Information on the ecology, physiology, and biology of the organism should be reviewed when assessing whether an organism is a reasonable surrogate of a commonly consumed organism.

g. BCFs may be based on measurement of radioactivity from radiolabeled parent compounds only when the BCF is intended to include metabolites, when there is confidence that there is no interference due to metabolites of the parent compounds, or when studies are conducted to determine the extent of metabolism, thus allowing for a proper correction.

h. The calculation of the BCF_T^t should appropriately address growth dilution, which can be particularly important in affecting BCF_T^t determinations for poorly depurated chemicals.

I. Other aspects of the methodology used should be similar to those described by the American Society of Testing and Materials (ASTM, 1999) and USEPA *Ecological Effects Test Guidelines* (USEPA, 1996).

j. In addition, the magnitude of the K_{ow} and the availability of corroborating BCF data should be considered. For example, if the steady-state method is used for the BCF_T^t determination, exposure periods longer than 28 days will generally be required for highly hydrophobic chemicals to reach steady state between the water and the organism.

k. If a baseline BCF_ℓ^{fd} derived from a laboratory-measured BCF_T^t consistently increases or decreases as the chemical concentration increases in the test solutions for the test organisms, the BCF_T^t should be selected from the test concentration(s) that would most closely correspond to the 304(a) criterion. Note: a BCF_T^t should not be calculated from a control treatment.

3. **Selecting Food Chain Multipliers.** An FCM reflects a chemical's tendency to biomagnify in the aquatic food web. Values of FCMs greater than 1.0 are indicative of biomagnification and typically apply to organic chemicals with log K_{ow} values between 4.0 and 9.0. For a given chemical, FCMs tend to be greater at higher trophic levels, although FCMs for trophic level three can be higher than those for trophic level four.

Food chain multipliers used to derive baseline BAF_ℓ^{fd}s using Procedure #1 can be selected from model-derived or field-derived estimates.

a. **Model-Derived FCMs.** For nonionic organic chemicals appropriate for Procedure #1, EPA has calculated FCMs for various K_{ow} values and trophic levels using the bioaccumulation model of Gobas (1993). The FCMs shown in Table 5-1 were calculated using the Gobas model as the ratio of the baseline BAF_ℓ^{fd}s for trophic levels 2, 3, and 4 to the baseline BCF_ℓ^{fd}.

EPA recommends using the biomagnification model by Gobas (1993) to derive FCMs for nonionic organic chemicals for several reasons. First, the Gobas model includes both benthic and pelagic food chains, thereby incorporating exposure of organisms to chemicals from both the sediment and the water column. Second, the input data needed to run the model can be readily defined. Third, the predicted BAFs using the model are in agreement with field-measured BAFs for chemicals, even those with very high log K_{ow}s. Finally, the model predicts chemical residues in benthic organisms using equilibrium partitioning theory, which is consistent with EPA's equilibrium partitioning sediment guidelines (USEPA, 2000d).

The Gobas model requires input of specific data on the structure of the food chain and the water quality characteristics of the water body of interest. For calculating national BAFs, a mixed pelagic/benthic food web structure consisting of four trophic levels is assumed. Trophic level 1 is phytoplankton, trophic level 2 is

zooplankton, trophic level 3 is forage fish (e.g., sculpin and smelt), and trophic level 4 are predatory fish (e.g., salmonids). Additional assumptions are made regarding the composition of the aquatic species' diets (e.g., salmonids consume 10 percent sculpin, 50 percent alewives, and 40 percent smelt), the physical parameters of the aquatic species (e.g., lipid values), and the water quality characteristics (e.g., water temperature, sediment organic carbon).

A mixed pelagic/benthic food web structure has been assumed for the purpose of calculating FCMs because it is considered to be most representative of the types of food webs that occur in aquatic ecosystems. FCMs derived using the mixed pelagic/benthic structure are also about mid-range in magnitude between a 100% pelagic and 100% benthic driven food web (see the Bioaccumulation TSD). The validity of FCMs derived using the mixed pelagic/benthic food web structure has

Table 5-1
Food-Chain Multipliers for Trophic Levels 2, 3 and 4
(Mixed Pelagic and Benthic Food Web Structure and $\prod_{socw} / K_{OW} = 23$)

Log K_{OW}	Trophic Level 2	Trophic Level 3	Trophic Level 4	Log K_{OW}	Trophic Level 2	Trophic Level 3	Trophic Level 4
4.0	1.00	1.23	1.07	6.6	1.00	12.9	23.8
4.1	1.00	1.29	1.09	6.7	1.00	13.2	24.4
4.2	1.00	1.36	1.13	6.8	1.00	13.3	24.7
4.3	1.00	1.45	1.17	6.9	1.00	13.3	24.7
4.4	1.00	1.56	1.23	7.0	1.00	13.2	24.3
4.5	1.00	1.70	1.32	7.1	1.00	13.1	23.6
4.6	1.00	1.87	1.44	7.2	1.00	12.8	22.5
4.7	1.00	2.08	1.60	7.3	1.00	12.5	21.2
4.8	1.00	2.33	1.82	7.4	1.00	12.0	19.5
4.9	1.00	2.64	2.12	7.5	1.00	11.5	17.6
5.0	1.00	3.00	2.51	7.6	1.00	10.8	15.5
5.1	1.00	3.43	3.02	7.7	1.00	10.1	13.3
5.2	1.00	3.93	3.68	7.8	1.00	9.31	11.2
5.3	1.00	4.50	4.49	7.9	1.00	8.46	9.11
5.4	1.00	5.14	5.48	8.0	1.00	7.60	7.23
5.5	1.00	5.85	6.65	8.1	1.00	6.73	5.58
5.6	1.00	6.60	8.01	8.2	1.00	5.88	4.19
5.7	1.00	7.40	9.54	8.3	1.00	5.07	3.07
5.8	1.00	8.21	11.2	8.4	1.00	4.33	2.20
5.9	1.00	9.01	13.0	8.5	1.00	3.65	1.54
6.0	1.00	9.79	14.9	8.6	1.00	3.05	1.06
6.1	1.00	10.5	16.7	8.7	1.00	2.52	0.721
6.2	1.00	11.2	18.5	8.8	1.00	2.08	0.483
6.3	1.00	11.7	20.1	8.9	1.00	1.70	0.320
6.4	1.00	12.2	21.6	9.0	1.00	1.38	0.210
6.5	1.00	12.6	22.8				

been evaluated in several different ecosystems including Lake Ontario, the tidally influenced Bayou D'Inde in Louisiana, the Fox River and Green Bay, Wisconsin, and the Hudson River in New York. Additional details of the validation of EPA's national default FCMs and the assumptions, uncertainties, and input parameters for the model are provided in the Bioaccumulation TSD.

Although EPA uses the FCMs in Table 5-1 to derive its national 304(a) criteria, EPA recognizes that food webs of other waterbodies might differ from the assumptions used to calculate national BAFs. In these situations, States and authorized Tribes may wish to use alternate food web structures for calculating FCMs for use in setting State or Tribal water quality criteria. Additional guidance on the use of alternate food web structures for calculating State, Tribal, or site-specific criteria is provided in the Bioaccumulation TSD.

b. **Field-Derived FCMs.** In addition to model-derived estimates of FCMs, field data may also be used to derive FCMs. Currently, the use of field-derived FCMs is the only method recommended for estimating FCMs for inorganic and organometalic chemicals because appropriate model-derived estimates are not yet available (see Section 5.6). In contrast to the model-based FCMs described previously, field-derived FCMs account for any metabolism of the chemical of concern by the aquatic organisms used to calculate the FCM.

Field-derived FCMs should be calculated using lipid-normalized concentrations of the nonionic organic chemical in appropriate predator and prey species using the following equations.

$$FCM_{TL2} = BMF_{TL2} \quad \text{(Equation 5-21)}$$

$$FCM_{TL3} = (BMF_{TL3})\,(BMF_{TL2}) \quad \text{(Equation 5-22)}$$

$$FCM_{TL4} = (BMF_{TL4})\,(BMF_{TL3})\,(BMF_{TL2}) \quad \text{(Equation 5-23)}$$

where:

FCM = Food chain multiplier for designated trophic level (TL2, TL3, or TL4)
BMF = Biomagnification factor for designated trophic level (TL2, TL3, or TL4)

The basic difference between FCMs and BMFs is that FCMs relate back to trophic level one (or trophic level two as assumed by the Gobas (1993) model), whereas BMFs always relate back to the next lowest trophic level. For nonionic organic chemicals, BMFs can be calculated from tissue residue concentrations determined in biota at a site according to the following equations.

$$BMF_{TL2} = (C_{\ell, TL2}) / (C_{\ell, TL1}) \quad \text{(Equation 5-24)}$$

$$BMF_{TL3} = (C_{\ell, TL3}) / (C_{\ell, TL2}) \quad \text{(Equation 5-25)}$$

$$BMF_{TL4} = (C_{\ell, TL4}) / (C_{\ell, TL3}) \quad \text{(Equation 5-26)}$$

where:

C_ℓ = Lipid-normalized concentration of chemical in tissue of appropriate biota that occupy the specified trophic level (TL2, TL3, or TL4)

In addition to the acceptability guidelines pertaining to field-measured BAFs, the following procedural and quality assurance requirements apply to field-measured FCMs.

(1) Information should be available to identify the appropriate trophic levels for the aquatic organisms and appropriate predator-prey relationships for the site from which FCMs are being determined. General information on determining trophic levels of aquatic organisms can be found in USEPA 2000a,b,c.

(2) The aquatic organisms sampled from each trophic level should reflect the most important exposure pathways leading to human exposure via consumption of aquatic organisms. For higher trophic levels (e.g., 3 and 4), aquatic species should also reflect those that are commonly consumed by humans.

(3) The studies from which the FCMs are derived should contain sufficient supporting information from which to determine that tissue samples were collected and analyzed using appropriate, sensitive, accurate, and precise methods.

(4) The percent lipid should be either measured or reliably estimated for the tissue used to determine the FCM.

(5) The tissue concentrations should reflect average exposure over the approximate time required to achieve steady-state in the target species.

D. Baseline BAF_ℓ^{fd} from a K_{ow} and FCM

The fourth method in Procedure #1 consists of using a K_{ow} and an appropriate FCM for estimating the baseline BAF_ℓ^{fd}. In this method, the K_{ow} is assumed to be equal to the baseline BCF_ℓ^{fd}. Numerous investigations have demonstrated a linear relationship between the logarithm of the BCF and the logarithm of the octanol-water partition coefficient (K_{ow}) for organic chemicals for fish and other aquatic organisms. Isnard and Lambert (1988) list various regression equations that illustrate this linear relationship. When the regression equations are constructed using lipid-normalized BCFs, the slopes and intercepts are not significantly different from one and zero, respectively (e.g., de Wolf, et al., 1992). The underlying assumption for the linear relationship between the BCF and K_{ow} is that the bioconcentration process can be viewed as the partitioning of a chemical between the lipid of the aquatic organisms and water and that the K_{ow} is a useful surrogate for this partitioning process (Mackay, 1982). To account for biomagnification, Procedure #1 requires the K_{ow} value be used in conjunction with an appropriate FCM.

1. **Baseline BAF_{ℓ}^{fd} Equation.** For each acceptable K_{ow} value and FCM for the chemical of concern, calculate a baseline BAF_{ℓ}^{fd} using the following equation.

$$\text{Baseline } BAF_{\ell}^{fd} = (FCM) \cdot (K_{ow}) \qquad \text{(Equation 5-27)}$$

where:

Baseline BAF_{ℓ}^{fd}	=	BAF expressed on a freely dissolved and lipid-normalized basis for a given trophic level
FCM	=	The food chain multiplier for the appropriate trophic level obtained from Table 5-1 by linear interpolation or from appropriate field data (used with Procedure #1 only)
K_{ow}	=	Octanol-water partition coefficient

The BCF-K_{ow} relationship has been developed primarily for nonionic organic chemicals that are not readily metabolized by aquatic organisms and thus is most appropriate for poorly-metabolized nonionic organic chemicals (i.e., Procedures #1 and #3 as depicted in Figure 5-1). For poorly-metabolized nonionic organic chemicals with large log K_{ow}s (i.e., > 6), reported log BCFs are often not equal to log K_{ow}. EPA believes that this nonlinearity is primarily due to not accounting for several factors which affect the BCF determination. These factors include not basing BCFs on the freely dissolved concentration in water, not accounting for growth dilution, not assessing BCFs at steady-state, inaccuracies in measurements of uptake and elimination rate constants, and complications from the use of solvent carriers in the exposure. Application of Equation 5-27 for predicting BAFs has been conducted in several different ecosystems including Lake Ontario, the tidally influenced Bayou D'Inde in Louisiana, the Fox River and Green Bay, Wisconsin, and the Hudson River in New York. Additional detail on the validation, technical basis, assumptions, and uncertainty associated with Equation 5-27 and is provided in the Bioaccumulation TSD.

2. **FCMs and K_{ow}s**. Food chain multipliers and K_{ow} values should be selected as described previously in Procedure #1.

5.4.3.2 Selecting Final Baseline BAF_{ℓ}^{fd}s

After calculating individual baseline BAF_{ℓ}^{fd}s using as many of the methods in Procedure #1 as possible, the next step is to determine a final baseline BAF_{ℓ}^{fd} for each trophic level from the individual baseline BAF_{ℓ}^{fd}s (see Figures 5-1 and 5-2). The final baseline BAF_{ℓ}^{fd} will be used in the last step to determine the national BAF for each trophic level. The final baseline BAF_{ℓ}^{fd} for each trophic level should be determined from the individual baseline BAF_{ℓ}^{fd}s by considering the data preference hierarchy defined by Procedure #1 and uncertainty in the data. The data preference hierarchy for Procedure #1 is (in order of preference):

1. a baseline BAF_{ℓ}^{fd} from an acceptable field-measured BAF (method 1)

2. a baseline BAF_{ℓ}^{fd} predicted from an acceptable field-measured BSAF (method 2),
3. a baseline BAF_{ℓ}^{fd} predicted from an acceptable BCF and FCM (method 3), or
4. a baseline BAF_{ℓ}^{fd} predicted from an acceptable K_{ow} and FCM (method 4).

This data preference hierarchy reflects EPA's preference for BAFs based on field-measurements of bioaccumulation (methods 1 and 2) over those based on laboratory-measurements and/or predictions of bioaccumulation (methods 3 and 4). However, this data preference hierarchy should not be considered inflexible. Rather, it should be used as a guide for selecting the final baseline BAF_{ℓ}^{fd}s when the uncertainty is similar among two or more baseline BAF_{ℓ}^{fd}s derived using different methods. The following steps and guidelines should be followed for selecting the final baseline BAF_{ℓ}^{fd}s using Procedure #1.

1. **Calculate Species-Mean Baseline BAF_{ℓ}^{fd}s.** For each BAF method where more than one acceptable baseline BAF_{ℓ}^{fd} is available for a given species, calculate a species-mean baseline BAF_{ℓ}^{fd} as the geometric mean of all available individual baseline BAF_{ℓ}^{fd}s. When calculating a species-mean baseline BAF_{ℓ}^{fd}, individual baseline BAF_{ℓ}^{fd}s should be reviewed carefully to assess the uncertainty in the BAF values. For highly hydrophobic chemicals applicable to Procedure #1, particular attention should be paid to whether sufficient spatial and temporal averaging of water and tissue concentrations was likely achieved in the BAF, BSAF, or BCF study. Highly uncertain baseline BAF_{ℓ}^{fd}s should not be used. Large differences in individual baseline BAF_{ℓ}^{fd}s for a given species (e.g., greater than a factor of 10) should be investigated further. In such cases, some or all of the baseline BAF_{ℓ}^{fd}s for a given species might not be used. Additional discussion on evaluating acceptability of BAF values is provided in the Bioaccumulation TSD.

2. **Calculate Trophic-Level-Mean Baseline BAF_{ℓ}^{fd}s.** For each BAF method where more than one acceptable species-mean baseline BAF_{ℓ}^{fd} is available within a given trophic level, calculate a trophic-level-mean baseline BAF_{ℓ}^{fd} as the geometric mean of acceptable species-mean baseline BAF_{ℓ}^{fd}s in that trophic level. Trophic-level-mean baseline BAF_{ℓ}^{fd}s should be calculated for trophic levels two, three, and four because available data on U.S. consumers of fish and shellfish indicate significant consumption of organisms in these trophic levels.

3. **Select a Final Baseline BAF_{ℓ}^{fd} for Each Trophic Level.** For each trophic level, select the final baseline BAF_{ℓ}^{fd} using best professional judgment by considering: (1) the data preference hierarchy shown previously, (2) the relative uncertainty in the trophic-level-mean baseline BAF_{ℓ}^{fd}s derived using different methods, and (3) the weight of evidence among the four methods.

    a. In general, when more than one trophic-level-mean baseline BAF_{ℓ}^{fd} is available for a given trophic level, the final trophic-level-mean baseline BAF_{ℓ}^{fd} should be selected from the most preferred BAF method defined by the data preference hierarchy for Procedure #1.

    b. If uncertainty in a trophic-level-mean baseline BAF based on a higher tier (more preferred) method is judged to be substantially greater than a trophic-level-mean

baseline BAF from a lower tier method, and the weight of evidence among the various methods suggests that a BAF value from lower tier method is likely to be more accurate, then the final baseline BAF_{ℓ}^{fd} should be selected using a trophic level-mean baseline BAF_{ℓ}^{fd} from a lower tier method.

c. When considering the weight of evidence among the various BAF methods, greater confidence in the final baseline BAF_{ℓ}^{fd} is generally assigned when BAFs from a greater number of methods are in agreement for a given trophic level. However, lack of agreement among methods does not necessarily indicate less confidence if such disagreements can be adequately explained. For example, if the chemical of concern is metabolized by aquatic organisms represented by a BAF value, one would expect disagreement between a field-measured BAF (the highest priority data) and a predicted BAF using a K_{ow} and model-derived FCM. Thus, field-measured BAFs should generally be given the greatest weight among methods because they reflect direct measures of bioaccumulation and incorporate any metabolism which might occur in the organism and its food web.

d. The above steps should be performed for each trophic level until a final baseline BAF_{ℓ}^{fd} is selected for trophic levels two, three, and four.

5.4.3.3 Calculating National BAFs

The last step in deriving a national BAF for each trophic level is to convert the final baseline BAF_{ℓ}^{fd} determined in the previous step to a BAF that reflects conditions to which the national 304(a) criteria will apply (Figure 5-2). Since a baseline BAF_{ℓ}^{fd} is by definition normalized by lipid content and expressed on a freely dissolved basis, it needs to be adjusted to reflect the lipid fraction of aquatic organisms commonly consumed in the U.S. and the freely dissolved fraction expected in U.S. bodies of water. Converting a final baseline BAF_{ℓ}^{fd} to a national BAF requires information on: (1) the percent lipid of the aquatic organisms commonly consumed by humans, and (2) the freely dissolved fraction of the chemical of concern that would be expected in the ambient waters of interest. For each trophic level, a national BAF should be determined from a final baseline BAF_{ℓ}^{fd} according to the following guidelines.

1. **National BAF Equation.** For each trophic level, calculate a national BAF using the following equation.

$$\text{National BAF}_{(TL\ n)} = [(\text{Final Baseline BAF}_{\ell}^{fd})_{TL\ n} \cdot (f_{\ell})_{TL\ n} + 1] \cdot (f_{fd}) \qquad \text{(Equation 5-28)}$$

where:

Final Baseline BAF_{ℓ}^{fd} = Final trophic-level-mean baseline BAF expressed on a freely dissolved and lipid-normalized basis for trophic level "n"

$f_{\ell(TL\ n)}$	=	Lipid fraction of aquatic species consumed at trophic level "n"
f_{fd}	=	Fraction of the total chemical in water that is freely dissolved

The technical basis of Equation 5-28 is provided in the Bioaccumulation TSD. Guidance for determining each component of Equation 5-28 is provided below.

2. **Determining the Final Baseline BAF_{ℓ}^{fd}.** The final trophic-level-mean baseline BAF_{ℓ}^{fd}s used in this equation are those which have been determined using the guidance presented in Section 5.4.3.2 for selecting the final baseline BAF_{ℓ}^{fd}s.

3. **Lipid Content of Commonly Consumed Aquatic Species.** As illustrated by Equation 5-28, the percent lipid of the aquatic species consumed by humans is needed to accurately characterize the potential exposure to a chemical from ingestion of aquatic organisms.

   a. **National Default Lipid Values.** For the purposes of calculating a national 304(a) criterion, the following national default values for lipid fraction should be used: 1.9% (for trophic level two organisms), 2.6% (for trophic level three organisms), and 3.0% (for trophic level four organisms).

      These national default values for lipid content reflect national per capita average patterns of fish consumption in the United States. Specifically, they were calculated using the consumption-weighted mean lipid content of commonly consumed fish and shellfish as identified by the USDA Continuing Survey of Food Intake by Individuals (CSFII) for 1994 through 1996. This same national survey data was used to derive national default values of fish consumption. To maintain consistency with the fish consumption assumptions, only freshwater and estuarine organisms were included in the derivation of the national default lipid values. Additional details on the technical basis, assumptions, and uncertainty in the national default values of lipid fraction are provided in the Bioaccumulation TSD.

      Although national default lipid values are used by EPA to set national 304(a) criteria, EPA encourages States and authorized Tribes to use local or regional data on lipid content of consumed aquatic species when adopting criteria into their water quality standards because local or regional consumption patterns (and lipid content) can differ from national consumption patterns. Additional guidance on developing site-specific values of lipid content, including a database of lipid content for many commonly consumed aquatic organisms, is found in the Bioaccumulation TSD.

4. **Freely Dissolved Fraction.** The third piece of information required for deriving a national BAF is the freely dissolved fraction of the chemical of concern that is expected

in waters of the United States. As noted previously, expressing BAFs on the freely dissolved concentration in water allows a common basis for averaging BAFs from several studies. However, for use in criteria development, these BAFs should be converted back to values based on the total concentration in the water to be consistent with monitored water column and effluent concentrations, which are typically based on total concentrations of chemicals in the water. This should be done by multiplying the freely dissolved baseline BAF_{ℓ}^{fd} by the fraction of the freely dissolved chemical expected in water bodies of the United States where criteria are to be applied, as shown in Equation 5-29.

$$f_{fd} = \frac{1}{[1 + (POC \cdot K_{ow}) + (DOC \cdot 0.08 \cdot K_{ow})]} \qquad \text{(Equation 5-29)}$$

where:

POC	=	national default value for the particulate organic carbon concentration (kg/L)
DOC	=	national default value for the dissolved organic carbon concentration (kg/L)
K_{ow}	=	n-octanol water partition coefficient for the chemical

Equation 5-29 is identical to Equation 5-12, which was used to determine the freely dissolved fraction for deriving baseline BAF_{ℓ}^{fd}s from field-measured BAFs. However, the POC and DOC concentrations used in Equation 5-29 reflect those values that are expected in U.S. bodies of water, not the POC and DOC values in the study water used to derive the BAF. Guidance for determining each component of Equation 5-29 follows.

a. **National Default Values of POC and DOC.** For estimating the freely dissolved fraction of the chemical of concern that is expected in U.S. water bodies, national default values of 0.5 mg/L (5×10^{-7} kg/L) for POC and 2.9 mg/L (2.9×10^{-6} kg/L) for DOC should be used. These values are 50th percentile values (medians) based on an analysis of over 110,000 DOC values and 85,000 POC values contained in EPA's STORET database from 1980 through 1999. These default values reflect a combination of values for streams, lakes and estuaries across the United States. Additional details on the technical basis, assumptions, and uncertainty in the derivation and application of the national default values of POC and DOC are provided in the Bioaccumulation TSD.

   Although national default values of POC and DOC concentrations are used by EPA to set national 304(a) criteria as described by this document, EPA encourages States and authorized Tribes to use local or regional data on POC and DOC when adopting criteria into their water quality standards. EPA encourages States and Tribes to consider local or regional data on POC and DOC because local or regional conditions may result in differences in POC or DOC

concentrations compared with the values used as national defaults. Additional guidance on developing local or regional values of POC and DOC, including a database of POC and DOC values segregated by waterbody type, is found in the Bioaccumulation TSD.

b. **K_{ow} Value.** The value selected for the K_{ow} of the chemical of concern should be the same value used in earlier calculations (e.g., for calculating baseline BAF_{ℓ}^{fd}s and FCMs). Guidance for selecting the K_{ow} value is found in the Bioaccumulation TSD.

5.4.4 Deriving National BAFs Using Procedure #2

This section provides guidance for calculating national BAFs for nonionic organic chemicals using Procedure #2 shown in Figure 5-1. The types of nonionic organic chemicals for which Procedure #2 is most appropriate are those that are classified as moderately to highly hydrophobic and subject to high rates of metabolism by aquatic biota (see Section 5.4.2 above). Non-aqueous contaminant exposure and subsequent biomagnification in aquatic food webs are not generally of concern for chemicals that are classified in this category. As a result, FCMs are not used in this procedure. In addition, K_{ow} -based predictions of bioconcentration are not used in this procedure since the K_{ow} /BCF relationship is primarily based on poorly metabolized chemicals. Some nonionic organic chemicals for which Procedure #2 is probably appropriate include certain PAHs which are believed to be metabolized substantially by fish (e.g., benzo[a]pyrene, phenanthrene, fluoranthene, pyrene, benzo[a]anthracene and chrysene/triphenylene; USEPA, 1980; Burkhard and Lukasewycz, 2000).

According to Procedure #2, the following three methods can be used in deriving a national BAF:

- using a BAF from an acceptable field study (i.e., a field-measured BAF) (method 1),
- predicting a BAF from an acceptable BSAF (method 2), and
- predicting a BAF from an acceptable BCF (method 3).

Each of these three methods relies on measured data for assessing bioaccumulation and therefore, includes the effects of chemical metabolism by the study organism in the BAF estimate. The field-measured BAF and BSAF methods also incorporate any metabolism which occurs in the aquatic food web.

As shown in Figure 5-2, the next steps in deriving a national BAF after selecting the derivation procedure are: (1) calculating individual baseline BAF_{ℓ}^{fd}s, (2) selecting the final baseline BAF_{ℓ}^{fd}s, and (3) calculating the national BAFs. Each of these three steps is discussed separately below.

5.4.4.1 Calculating Individual Baseline BAF_{ℓ}^{fd}s

As described previously in Procedure #1, calculating individual baseline BAF_{ℓ}^{fd}s involves normalizing the measured BAF_{T}^{t} or BCF_{T}^{t} (which are based on the total chemical in water and

tissue) by the lipid content of the study organisms and the freely dissolved fraction of the chemical in the study water. Converting measured BAF_T^t (or BCF_T^t) values to baseline BAF_ℓ^{fd} (or BCF_ℓ^{fd}) values is designed to account for variation in measured BAF_T^ts that is caused by differences in lipid content of study organisms and differences in the freely dissolved fraction of chemical in study waters. Therefore, baseline BAF_ℓ^{fd}s are considered more amenable for extrapolating and averaging BAFs across different species and different study waters compared with total BAF_T^ts.

1. For each species where acceptable data are available, calculate all possible baseline BAF_ℓ^{fd}s using each of the three methods shown above for Procedure #2.

2. Individual baseline BAF_ℓ^{fd}s should be calculated from field-measured BAF_T^ts, field-measured BSAFs, and laboratory BCF_T^ts according to the following procedures.

A. Baseline BAF_ℓ^{fd} from Field-Measured BAFs

1. Except where noted below, a baseline BAF_ℓ^{fd} should be calculated from a field-measured BAF_T^t using the guidance and equations outlined in Section 5.4.3.1(A) for determining baseline BAF_ℓ^{fd}s from field-measured BAFs in Procedure #1.

2. Because nonionic organic chemicals applicable to Procedure #2 have relatively high rates of metabolism in aquatic organisms, they will tend to reach steady state more quickly than nonionic organic chemicals with similar K_{ow} values but which undergo little or no metabolism. Therefore, less temporal averaging of chemical concentrations would generally be required for determining field-measured BAF_T^ts with highly metabolizable chemicals compared with chemicals that are poorly metabolized by aquatic biota.

B. Baseline BAF_{ℓ}^{fd} Derived from Field-measured BSAFs

1. A baseline BAF_{ℓ}^{fd} should be calculated from a field-measured BSAF using the guidance and equations outlined in Section 5.4.3.1(B) for determining baseline BAF_{ℓ}^{fd}s from field-measured BSAFs in Procedure #1.

C. Baseline BAF_{ℓ}^{fd} from a Laboratory-Measured BCF

1. Except where noted below, a baseline BAF_{ℓ}^{fd} should be calculated from a laboratory-measured BCF_{T}^{t} using the guidance and equations outlined in Section 5.4.3.1(c) for determining baseline BAF_{ℓ}^{fd}s from a laboratory-measured BCF and FCM in Procedure #1.

2. Because biomagnification is not an overriding concern for nonionic organic chemicals applicable to Procedure #2, food chain multipliers are not used in the derivation of a baseline BAF_{ℓ}^{fd} from a laboratory-measured BCF_{T}^{t} .

5.4.4.2 Selecting Final Baseline BAF_{ℓ}^{fd}s

After calculating individual, baseline BAF_{ℓ}^{fd}s using as many of the methods in Procedure #2 as possible, the next step is to determine a final baseline BAF_{ℓ}^{fd} for each trophic level from the individual baseline BAF_{ℓ}^{fd}s. The final baseline BAF_{ℓ}^{fd} will be used in the last step to determine the national BAF for each trophic level. A final baseline BAF_{ℓ}^{fd} for each trophic level should be determined from the individual baseline BAF_{ℓ}^{fd}s by considering the data preference hierarchy defined by Procedure #2 and uncertainty in the data. The data preference hierarchy for Procedure #2 is (in order of preference):

1. a baseline BAF_{ℓ}^{fd} from an acceptable field-measured BAF (method 1),
2. a baseline BAF_{ℓ}^{fd} from an acceptable field-measured BSAF (method 2), or
3. a baseline BAF_{ℓ}^{fd} from an acceptable laboratory-measured BCF (method 3).

This data preference hierarchy reflects EPA's preference for BAFs based on field-measurements of bioaccumulation (methods 1 and 2) over those based on laboratory-measurements (method 3). However, as explained in Procedure #1, this data preference hierarchy should not be considered inflexible. Rather, it should be used as a guide for selecting the final baseline BAF_{ℓ}^{fd}s when the underlying uncertainty is similar among two or more baseline BAF_{ℓ}^{fd}s derived using different methods. Although biomagnification is not generally a concern for chemicals subject to Procedure #2, trophic level differences in bioaccumulation might be substantial to the extent that the rate of chemical metabolism by organisms in different trophic levels differs. For example, certain PAHs have been shown to be metabolized to a much greater extent by some fish compared with some invertebrate species (James, 1989). Therefore, final baseline BAF_{ℓ}^{fd}s for chemicals applicable to Procedure #2 should be determined on a trophic-level-specific basis according to the following guidelines.

1. The final baseline BAF_{ℓ}^{fd}s in Procedure #2 should be selected according to the same steps described in Procedure #1 but with the substitution of the data preference hierarchy described above for Procedure #2. Specifically, the species-mean baseline BAF_{ℓ}^{fd}s,

trophic-level-mean baseline BAF_{ℓ}^{fd}s, and the final baseline BAF_{ℓ}^{fd}s should be determined according to the guidelines presented in Procedure #1 (Section 5.4.3.2, Steps 1, 2, and 3).

5.4.4.3 Calculating the National BAFs

As described in Procedure #1, the last step in deriving national BAFs for nonionic organic chemicals is to convert the final baseline BAF_{ℓ}^{fd}s determined in the previous step to BAFs which reflect conditions to which the national 304(a) criteria will apply (Figure 5-2).

1. For trophic levels two, three, and four, national BAFs should be calculated from the final baseline BAF_{ℓ}^{fd}s using the same equation and procedures described previously in Procedure #1 (see Section 5.4.3.3 entitled "Calculating the National BAFs").

5.4.5 Deriving National BAFs Using Procedure #3

This section provides guidance for calculating national BAFs for nonionic organic chemicals using Procedure #3 shown in Figure 5-1. The types of nonionic organic chemicals for which Procedure #3 is most appropriate are those that are classified as low in hydrophobicity (i.e., log K_{ow} values less than 4.0) and subject to low (or unknown) rates of metabolism by aquatic biota (see Section 5.4.2 above). Non-aqueous contaminant exposure and subsequent biomagnification in aquatic food webs are not generally of concern for chemicals that are classified in this category (Fisk et al., 1998; Gobas et al., 1993; Connolly and Pedersen, 1988; Thomann, 1989). As a result, FCMs are not used in this procedure.

According to Procedure #3, the following three methods can be used in deriving a national BAF:

- using a BAF from an acceptable field study (i.e., a field-measured BAF),
- predicting a BAF from an acceptable laboratory-measured BCF, and
- predicting a BAF from an acceptable K_{ow}.

After selecting the derivation procedure, the next steps in deriving a national BAF at a given trophic level for nonionic organic chemicals are: (1) calculating individual baseline BAF_{ℓ}^{fd}s, (2) selecting the final baseline BAF_{ℓ}^{fd}, and (3) calculating the national BAF (Figure 5-2). Each of these three steps is discussed separately below.

5.4.5.1 Calculating Individual Baseline BAF_{ℓ}^{fd}s

Calculating individual baseline BAF_{ℓ}^{fd}s involves normalizing each measured BAF_{T}^{t} or BCF_{T}^{t} (which are based on the total chemical in water and tissue) by the lipid content of the study organism and the freely dissolved fraction of the chemical in the study water. For additional discussion of the technical basis for calculating baseline BAF_{ℓ}^{fd}s, see Section 5.4.3.1 in Procedure #1.

1. For each species where acceptable data are available, calculate all possible baseline BAF_{ℓ}^{fd}s using each of the three methods shown above for Procedure #3.

2. An individual baseline BAF_{ℓ}^{fd} should be calculated from field-measured BAF_{T}^{t}s, laboratory-measured BCF_{T}^{t}s, and K_{ow} values according to the following procedures.

A. Baseline BAF_{ℓ}^{fd} from Field-Measured BAFs

1. Except where noted below, a baseline BAF_{ℓ}^{fd} should be calculated from a field-measured BAF_{T}^{t} using the guidance and equations outlined in Section 5.4.3.1(A) in Procedure #1.

2. **Freely Dissolved Fraction**. Due to their low hydrophobicity (i.e., log K_{ow} < 4.0), nonionic organic chemicals applicable to Procedure #3 are expected to remain almost entirely in the freely dissolved form in natural waters with dissolved and particulate organic carbon concentrations typical of most field BAF studies. Therefore, the freely dissolved fraction should be assumed to be equal to 1.0, unless the concentrations of DOC and POC are very high in the field BAF study. For studies with very high DOC or POC concentrations, (e.g., about 100 mg/L or higher for DOC or 10 mg/L or higher for POC), the freely dissolved fraction may be substantially lower than 1.0 and therefore should be calculated using Equation 5-12.

3. **Temporal Averaging of Concentrations.** Also due to their low hydrophobicity, nonionic organic chemicals appropriate to Procedure #3 will also tend to reach steady state quickly compared with those chemicals to which Procedure #1 applies. Therefore, the extent of temporal averaging of tissue and water concentrations is typically much less than that required for highly hydrophobic chemicals to which Procedure #1 is applied. In addition, field studies used to calculate BAFs for these chemicals should have sampled water and tissue at similar points in time because tissue concentrations respond more rapidly to changes in water concentrations. EPA will be providing additional guidance on appropriate BAF study designs for nonionic organic chemicals (including those appropriate to Procedure #3) in its forthcoming guidance document on conducting field BAF and BSAF studies.

B. Baseline BAF_{ℓ}^{fd} from a Laboratory-Measured BCF

1. Except where noted below, a baseline BAF_{ℓ}^{fd} should be calculated from a laboratory-measured BCF_{T}^{t} using the guidance and equations outlined in Section 5.4.3.1(c) of Procedure #1.

2. **Food Chain Multipliers.** Because biomagnification is not an overriding concern for the minimally hydrophobic chemicals applicable to Procedure #3, FCMs are not used in the derivation of a baseline BAF_{ℓ}^{fd} from a laboratory-measured BCF_{T}^{t}.

3. **Freely Dissolved Fraction**. Due to their low hydrophobicity (i.e., log K_{ow} < 4.0), nonionic organic chemicals to which Procedure #3 is applied are expected to remain

almost entirely in the freely dissolved form in waters containing dissolved and particulate organic carbon concentrations typical of laboratory BCF studies. Therefore, the freely dissolved fraction should usually be assumed equal to 1.0. The freely dissolved fraction will be substantially less than 1.0 only in situations where unusually high concentrations of DOC and POC are present in the laboratory BCF study (e.g., above about 100 mg/L for DOC or about 10 mg/L for POC). In this situation, the freely dissolved fraction should be calculated according to Equation 5-12.

C. Baseline BAF_{ℓ}^{fd} from a K_{ow}

1. Except where noted below, a baseline BAF_{ℓ}^{fd} should be calculated from an acceptable K_{ow} using the guidance and equations outlined in Section 5.4.3.1(D) in Procedure #1.

2. Because biomagnification is not an overriding concern for nonionic organic chemicals with low hydrophobicity (i.e., log K_{ow} < 4.0), food chain multipliers are not used in Procedure #3 for deriving the baseline BAF_{ℓ}^{fd} from a K_{ow}.

5.4.5.2 Selecting Final Baseline BAF_{ℓ}^{fd}s

After calculating individual baseline BAF_{ℓ}^{fd}s using as many of the methods in Procedure #3 as possible, the next step is to determine a final baseline BAF_{ℓ}^{fd} for each trophic level from the individual baseline BAF_{ℓ}^{fd}s (Figure 5-2). The final baseline BAF_{ℓ}^{fd} will be used in the last step to determine the national BAF for each trophic level. The final baseline BAF_{ℓ}^{fd} for each trophic level should be determined from the individual baseline BAF_{ℓ}^{fd}s by considering the data preference hierarchy defined by Procedure #3 and uncertainty in the data. The data preference hierarchy for Procedure #3 is (in order of preference):

1. a baseline BAF_{ℓ}^{fd} from an acceptable field-measured BAF or laboratory-measured BCF, or
2. a baseline BAF_{ℓ}^{fd} predicted from an acceptable K_{ow} value.

This data preference hierarchy reflects EPA's preference for BAFs that are based on measured data (field-measured BAFs and laboratory-measured BCFs) over BAFs based on predictive methods (K_{ow}). This data preference hierarchy should be used as a guide for selecting the final baseline BAF_{ℓ}^{fd}s when the uncertainty is similar among two or more baseline BAF_{ℓ}^{fd}s derived using different methods. Since bioaccumulation via dietary uptake and subsequent biomagnification generally are not of concern for chemicals subject to Procedure #3, field-measured BAFs and laboratory-measured BCFs are considered equally in determining the national BAF.

Final baseline BAF_{ℓ}^{fd}s should be selected for each trophic level using the following steps and guidelines.

1. **Calculate Species-Mean Baseline BAF_{ℓ}^{fd}s.** For each BAF method (i.e., field-measured BAF, BAF from a lab-measured BCF, or BAF from a K_{ow}) where more than one

acceptable baseline BAF_{ℓ}^{fd} is available for a given species, calculate a species-mean baseline BAF_{ℓ}^{fd} according to the guidance described previously in Procedure #1.

2. **Calculate Trophic-Level-Mean Baseline BAF_{ℓ}^{fd}s.** For each BAF method where more than one acceptable species-mean baseline BAF_{ℓ}^{fd} is available within a given trophic level, calculate the trophic-level-mean baseline BAF_{ℓ}^{fd} as the geometric mean of acceptable species-mean baseline BAF_{ℓ}^{fd}s in that trophic level.

3. **Select a Final Baseline BAF_{ℓ}^{fd} for Each Trophic Level.** For each trophic level, select the final baseline BAF_{ℓ}^{fd} using best professional judgment by considering: (1) the data preference hierarchy, (2) the relative uncertainties among trophic-level-mean baseline BAF_{ℓ}^{fd}s derived using different methods, and (3) the weight of evidence among the three methods.

    a. In general, when more than one trophic-level-mean baseline BAF_{ℓ}^{fd} is available within a given trophic level, the final baseline BAF_{ℓ}^{fd} should be selected from the most preferred BAF method defined by the data preference hierarchy for Procedure #3. Within the first data preference tier, field-measured BAFs and laboratory-measured BCFs are considered equally desirable for deriving a final trophic-level-mean baseline BAF_{ℓ}^{fd} using Procedure #3. If a trophic-level-mean baseline BAF_{ℓ}^{fd} is available from both a field-measured BAF and a laboratory-measured BCF, the final baseline BAF_{ℓ}^{fd} should be selected using the trophic-level-mean baseline BAF_{ℓ}^{fd} or BCF_{ℓ}^{fd} with the least overall uncertainty.

    b. If uncertainty in a trophic-level-mean baseline BAF_{ℓ}^{fd} based on a higher tier (more preferred) method is judged to be substantially greater than a trophic-level-mean baseline BAF_{ℓ}^{fd} from a lower tier method, then the final baseline BAF_{ℓ}^{fd} should be selected using a trophic-level-mean baseline BAF_{ℓ}^{fd} from a lower tier method.

    c. The above steps should be performed for each trophic level until a final baseline BAF_{ℓ}^{fd} is selected for trophic level two, three, and four.

5.4.5.3 Calculating the National BAFs

As described in Procedure #1, the last step in deriving a national BAF for a given trophic level for nonionic organic chemicals is to convert the final baseline BAF_{ℓ}^{fd} determined in the previous step to a BAF that reflect conditions to which the national 304(a) criterion will apply (Figure 5-2). Each national BAF should be determined from a final baseline BAF_{ℓ}^{fd} according to the following guidelines.

1. **National BAF Equation.** Except where noted below, national BAFs for trophic levels two, three, and four should be calculated from the final, trophic-level-mean baseline BAF_{ℓ}^{fd}s using Equation 5-28 and associated guidance described in Procedure #1 (see Section 5.4.3.3).

2. **Freely Dissolved Fraction**. Due to their low hydrophobicity (i.e., log K_{ow} < 4.0), a freely dissolved fraction of 1.0 should be assumed for calculating national BAFs for nonionic organic chemicals using Procedure #3. A freely dissolved fraction of 1.0 should be assumed because at a log K_{ow} of less than 4.0, nonionic organic chemicals are expected to remain over 99 percent in the freely dissolved form at POC and DOC concentrations corresponding to national default values for U.S. bodies of water (i.e., 0.5 mg/L and 2.9 mg/L, respectively).

5.4.6 Deriving National BAFs Using Procedure #4

This section provides guidance for calculating national BAFs for nonionic organic chemicals using Procedure #4 shown in Figure 5-1. The types of nonionic organic chemicals for which Procedure #4 is most appropriate are those that are classified as having low hydrophobicity and subject to high rates of metabolism by aquatic biota (see Section 5.4.2 above). Non-aqueous contaminant exposure and subsequent biomagnification in aquatic food webs are not generally of concern for chemicals that are classified in this category. As a result, FCMs are not used in this procedure. In addition, K_{ow} -based predictions of bioconcentration are not used in this procedure since the K_{ow} /BCF relationship is primarily based on poorly metabolized chemicals. One example of a nonionic organic chemical for which Procedure #4 appears appropriate is butyl benzyl phthalate in fish. Using radiolabeling techniques with confirmation by chromatographic analysis, Carr et al. (1997) present evidence that indicates butyl benzyl phthalate is extensively metabolized in sunfish. Carr et al. (1997) also report measured BCFs (and subsequently lipid-normalized BCFs) which are substantially below predicted BCFs based on log $K_{ow.}$ In a study of chlorinated anilines (which would be essentially un-ionized at ambient pH), de Wolf et al. (1992) reported measured BCFs substantially lower than those predicted based on K_{ow}. The authors suggested that biotransformation (metabolism) involving the amine (NH_2) was responsible for the lower measured BCFs.

According to Procedure #4, the following two methods can be used in deriving a national BAF:

- using a BAF from an acceptable field study (i.e., a field-measured BAF), and
- predicting a BAF from an acceptable BCF.

After selecting the derivation procedure, the next steps in deriving a national BAF for a given trophic level for nonionic organic chemicals are: (1) calculating individual baseline BAF_{ℓ}^{fd}s, (2) selecting the final baseline BAF_{ℓ}^{fd}, and (3) calculating the national BAF (Figure 5-2). Each of these three steps is discussed separately below.

5.4.6.1 Calculating Individual Baseline BAF_{ℓ}^{fd}s

Calculating individual baseline BAF_{ℓ}^{fd}s involves normalizing the measured BAF_T^t or BCF_T^t (which are based on the total chemical in water and tissue) by the lipid content of the study organism and the freely dissolved fraction of the chemical in the study water. For additional discussion of the technical basis for calculating baseline BAF_{ℓ}^{fd}s, see Section 5.4.3.1 in Procedure #1.

1. For each species where acceptable data are available, calculate all possible baseline BAF_{ℓ}^{fd}s using each of the two methods shown above for Procedure #4.

2. Individual baseline BAF_{ℓ}^{fd}s should be calculated from field-measured BAF_{T}^{t}s and laboratory-measured BCF_{T}^{t}s according to the following procedures.

A. Baseline BAF_{ℓ}^{fd} from Field-Measured BAFs

1. A baseline BAF_{ℓ}^{fd} should be calculated from a field-measured BAF_{T}^{t} using the guidance and equations outlined in Section 5.4.3.1(A) in Procedure #1.

2. **Freely Dissolved Fraction**. Due to their low hydrophobicity (i.e., log K_{ow} < 4.0), nonionic organic chemicals applicable to Procedure #4 are expected to remain almost entirely in the freely dissolved form in natural waters with dissolved and particulate organic carbon concentrations typical of most field BAF studies. Therefore, the freely dissolved fraction should be assumed equal to 1.0 unless the concentrations of DOC and POC are very high in the field BAF study. For studies with very high DOC or POC concentrations, (e.g., about 100 mg/L or higher for DOC or 10 mg/L or higher for POC), the freely dissolved fraction may be substantially lower than 1.0 and therefore should be calculated using Equation 5-12.

3. **Temporal Averaging of Concentrations.** Also due to their low hydrophobicity, nonionic organic chemicals appropriate to Procedure #4 will also tend to reach steady-state quickly compared with those chemicals to which Procedure #1 applies. Therefore, the extent of temporal averaging of tissue and water concentrations is typically much less than that required for highly hydrophobic chemicals to which Procedure #1 is applied. In addition, field studies used to calculate BAFs for these chemicals should have sampled water and tissue at similar points in time because tissue concentrations should respond rapidly to changes in water concentrations. EPA will be providing additional guidance on appropriate BAF study designs for nonionic organic chemicals (including those appropriate to Procedure #4) in its forthcoming guidance document on conducting field BAF and BSAF studies.

B. Baseline BAF_{ℓ}^{fd} from a Laboratory-Measured BCF

1. Except where noted below, a baseline BAF_{ℓ}^{fd} should be calculated from a laboratory-measured BCF_{T}^{t} using the guidance and equations outlined in Section 5.4.3.1(c) of Procedure #1.

2. **Food Chain Multipliers.** Because biomagnification is not an important concern for the minimally hydrophobic chemicals applicable to Procedure #4, FCMs are not used in the derivation of a baseline BAF_{ℓ}^{fd} from a laboratory-measured BCF_{T}^{t}.

3. **Freely Dissolved Fraction**. Due to their low hydrophobicity (i.e., log K_{ow} < 4.0), nonionic organic chemicals to which Procedure #4 is applied are expected to remain

almost entirely in the freely dissolved form in waters containing dissolved and particulate organic carbon concentrations typical of laboratory BCF studies. Therefore, the freely dissolved fraction should usually be assumed to be equal to 1.0. The freely dissolved fraction will be substantially less than 1.0 only in situations where unusually high concentrations of DOC and POC are present in the lab BCF study (e.g., above about 100 mg/L for DOC or about 10 mg/L for POC). In this situation, the freely dissolved fraction should be calculated according to Equation 5-12.

5.4.6.2 Selecting Final Baseline BAF_{ℓ}^{fd}s

After calculating individual baseline BAF_{ℓ}^{fd}s using as many of the methods in Procedure #4 as possible, the next step is to determine a final baseline BAF_{ℓ}^{fd} for a given trophic level from the individual baseline BAF_{ℓ}^{fd}s (Figure 5-2). The final baseline BAF_{ℓ}^{fd} will be used in the last step to determine the national BAF for each trophic level. A final baseline BAF_{ℓ}^{fd} should be determined for each trophic level from the individual baseline BAF_{ℓ}^{fd}s by considering the data preference hierarchy defined by Procedure #4 and uncertainty in the data. The data preference hierarchy for Procedure #4 is:

1. a baseline BAF_{ℓ}^{fd} from an acceptable field-measured BAF or predicted from an acceptable laboratory-measured BCF.

Since bioaccumulation via dietary uptake and subsequent biomagnification generally are not of concern for chemicals subject to Procedure #4, field-measured BAFs and laboratory-measured BCFs are considered equally in determining the national BAF.

Final baseline BAF_{ℓ}^{fd}s should be selected for each trophic level using the following steps and guidelines.

1. **Calculate Species-Mean Baseline BAF_{ℓ}^{fd}s.** For each BAF method (i.e., field-measured BAF or a BAF from a lab-measured BCF) where more than one acceptable baseline BAF_{ℓ}^{fd} is available for a given species, calculate a species-mean baseline BAF_{ℓ}^{fd} according to the guidance described previously in Procedure #1.

2. **Calculate Trophic-Level-Mean Baseline BAF_{ℓ}^{fd}s.** For each BAF method where more than one acceptable species-mean baseline BAF_{ℓ}^{fd} is available within a given trophic level, calculate the trophic-level-mean baseline BAF_{ℓ}^{fd} as the geometric mean of acceptable species-mean baseline BAF_{ℓ}^{fd}s for that trophic level.

3. **Select a Final Baseline BAF_{ℓ}^{fd} for Each Trophic Level.** For each trophic level, select the final baseline BAF_{ℓ}^{fd} using best professional judgment by considering: (1) the data preference hierarchy, and (2) the relative uncertainties among trophic-level-mean BAFs derived using different methods.

    a. As discussed above, field-measured BAFs and laboratory-measured BCFs are considered equally desirable for deriving a final trophic-level-mean baseline

BAF_{ℓ}^{fd} using Procedure #4. If a trophic-level-mean baseline BAF_{ℓ}^{fd} is available from both a field-measured BAF and a laboratory-measured BCF, the final baseline BAF_{ℓ}^{fd} should be selected using the trophic-level-mean baseline BAF_{ℓ}^{fd} or BCF_{ℓ}^{fd} with the least overall uncertainty.

b. The above steps should be performed for each trophic level until a final baseline BAF_{ℓ}^{fd} is selected for trophic levels two, three, and four.

5.4.6.3 Calculating National BAFs

As described in Procedure #1, the last step in deriving a national BAF for a given trophic level for nonionic organic chemicals is to convert the final baseline BAF_{ℓ}^{fd} determined in the previous step to a BAF that reflects conditions to which the national 304(a) criterion will apply (Figure 5-2). Each national BAF should be determined from a final baseline BAF_{ℓ}^{fd} according to the following guidelines.

1. **National BAF Equation.** Except where noted below, national BAFs for trophic-levels two, three, and four should be calculated from the final, trophic-level-mean baseline BAF_{ℓ}^{fd}s using the same equation and procedures described previously in Procedure #1 (see Section 5.4.3.3 in Procedure #1).

2. **Freely Dissolved Fraction**. Due to their low hydrophobicity (i.e., log $K_{ow} < 4.0$), a freely dissolved fraction of 1.0 should be assumed for calculating national BAFs for nonionic organic chemicals using Procedure #4. A freely dissolved fraction of 1.0 should be assumed because at a log K_{ow} value of less than 4.0, nonionic organic chemicals are expected to remain over 99 percent in the freely dissolved form at POC and DOC concentrations corresponding to national default values for U.S. bodies of water (i.e., 0.5 mg/L and 2.9 mg/L, respectively).

5.5 NATIONAL BIOACCUMULATION FACTORS FOR IONIC ORGANIC CHEMICALS

This section contains guidelines for deriving national BAFs for ionic organic chemicals (i.e., organic chemicals which undergo significant ionization in water). As defined in Section 5.3.5, ionic organic chemicals contain functional groups which can either readily donate protons (e.g., organic acids with hydroxyl, carboxylic, and sulfonic groups) or readily accept protons (e.g., organic bases with amino and aromatic heterocyclic nitrogen groups). Some examples of ionic organic compounds include:

- chlorinated phenols (e.g., 2,4,6-trichlorophenol, pentachlorophenol),
- chlorinated phenoxyalkanoic acids (e.g., 2,4-dichlorophenoxyacetic acid [2,4-D]),
- nitrophenols (e.g., 2-nitrophenol, 2,4,6-trinitrophenol),
- cresols (e.g., 2,4-dinitro-*o*-cresol [DNOC]),
- pyridines (e.g., 2,4-dimethypyidine),
- aliphatic and aromatic amines (e.g., trimethylamine, aniline), and

- linear alkylbenzenesulfonate (LAS) surfactants.

Ionic organic chemicals are considered separately for deriving national BAFs because the anionic or cationic species of these chemicals behave much differently in the aquatic environment compared with their neutral (un-ionized) counterparts. The neutral species of ionic organic chemicals are thought to behave in a similar manner as nonionic organic compounds (e.g., partitioning to lipids and organic carbon as a function of hydrophobicity). However, the ionized (cationic, anionic) species exhibit a considerably more complex behavior involving multiple environmental partitioning mechanisms (e.g., ion exchange, electrostatic, and hydrophobic interactions) and a dependency on pH and other factors including ionic strength and ionic composition (Jafvert et al., 1990; Jafvert 1990; Schwarzenbach, et al., 1993). As a consequence, methods to predict the environmental partitioning of organic cations and anions are less developed and validated compared with methods for nonionic organic chemicals (Spacie, 1994; Suffet et al., 1994).

Given the current limitations in the state of the science for predicting the partitioning and bioaccumulation of the ionized species of ionic organic chemicals, procedures for deriving national BAFs for these chemicals differ depending on the extent to which the fraction of the total chemical is likely to be represented by the ionized (cationic, anionic) species in U.S. surface waters. When a significant fraction of the total chemical concentration is expected to be present as the ionized species in water, procedures for deriving the national BAF rely on empirical (measured) methods (i.e., Procedures #5 and 6 in Section 5.6). When an insignificant fraction of the total chemical is expected to be present as the ionized species (i.e., the chemical exists essentially in the neutral form), procedures for deriving the national BAF will follow those established for nonionic organic chemicals (e.g., Procedures #1 through #4 in Section 5.4). The following guidelines apply for assessing the occurrence of cationic and anionic forms at typical environmental pH ranges.

1. For the ionic organic chemical of concern, the dissociation constant, pK_a, should be compared to the range of pH values expected in fresh and estuarine waters of the U.S. At pH equal to the pK_a, 50% of the organic acid or base is expected to be present in the ionized species. The pH values for U.S. fresh and estuarine waters typically range between 6 and 9, although somewhat higher and lower values can occur in some bodies of water (e.g., acidic bogs and lakes, highly alkaline and eutrophic systems, etc.).

2. For organic acids, the chemical will exist almost entirely in its un-ionized form when pH is about 2 or more units below the pK_a. For organic bases, the chemical will exist almost entirely in its un-ionized form when pH is about 2 or more units above the pK_a. In these cases, the aqueous behavior of the chemical would be expected to be similar to nonionic organic chemicals. Therefore, national BAF should usually be derived using Procedures #1 through #4 in Section 5.4.

3. When pH is greater than the pK_a minus 2 for organic acids (or less than the pKa plus 2 for organic bases), the fraction of the total chemical that is expected to exist in its ionized form can become significant (i.e., $\geq$1% in the ionized). In these cases, the national BAF should usually be derived using Procedures #5 and #6 in Section 5.6.

4. In general, most organic acids (e.g., pentachlorophenol and silvex), exist primarily in the ionized form in ambient waters because their pK_a's (4.75 and 3.07, respectively) are much smaller than the pH of the ambient waters. Conversely, most organic bases, (e.g., aniline) exist mostly in the un-ionized form in ambient waters because their pK_a's (4.63 for aniline) are much smaller than the pH of the ambient waters.

5. The above guidelines are intended to be a general guide for deriving national BAFs for ionic organic chemicals, not an inflexible rule. Modifications to these guidelines should be considered on a case-by-case basis, particularly when such modifications are strongly supported by measured bioaccumulation or bioconcentration data. For example, initial models have been developed for predicting the solid and organic-phase partitioning of certain organic acids (e.g., Jafvert 1990, Jafvert et al., 1990). As these or other models become more fully developed and appropriately validated in the future, they should be considered in the development of national BAFs. In addition, since pH is a controlling factor for dissociation and subsequent partitioning of ionic organic chemicals, consideration should be given to expressing BAFs or BCFs as a function of pH (or other factors) where sufficient data exist to reliably establish such relationships.

5.6 NATIONAL BIOACCUMULATION FACTORS FOR INORGANIC AND ORGANOMETALLIC CHEMICALS

This section contains guidelines for deriving national BAFs for inorganic and organometallic chemicals as defined in Section 5.3.5. The derivation of BAFs for inorganic and organometallic chemicals differs in several ways from procedures for nonionic organic chemicals. First, lipid normalization of chemical concentrations in tissues does not generally apply for inorganic and organometallic chemicals. Thus, BAFs and BCFs cannot be extrapolated from one tissue to another based on lipid-normalized concentrations as is done for nonionic organic chemicals. Second, the bioavailability of inorganics and organometallics in water tends to be chemical-specific and thus, the techniques for expressing concentrations of nonionic organic chemicals based on the freely dissolved form do not generally apply. Third, at the present time there are no generic bioaccumulation models that can be used to predict BAFs for inorganic and organometallic chemicals as a whole, unlike the existence of K_{ow}-based models for nonionic organic chemicals. While some chemical-specific bioaccumulation models have been developed for inorganic and organometallic chemicals (e.g., Mercury Cycling Model by Hudson et. al, 1994), those models currently tend to require site-specific data for input to the model and are restricted to site-specific applications. As the models become more fully developed and validated in the future, they should be considered on a case-by-case basis in conjunction with the following procedures for deriving national BAFs.

5.6.1 Selecting the BAF Derivation Procedure

As shown in Figure 5-1, national BAFs can be derived using two procedures for inorganic and organometallic chemicals (Procedures #5 and #6). The choice of the BAF derivation procedure depends on whether or not the chemical undergoes biomagnification in aquatic food webs.

1. For many inorganic and organometallic chemicals, biomagnification does not occur and the BCF will be equal to the BAF. For these types of chemicals, Procedure #5 should be used to derive the national BAF. Procedure #5 considers BAFs and BCFs to be of equal value in determining the national BAF and does not require the use of FCMs with BCF measurements. Guidance for deriving BAFs using Procedure #5 is provided in Section 5.6.3.

2. For some inorganic and organometallic chemicals (e.g., methylmercury), biomagnification does occur and Procedure #6 should be used to determine the national BAF. Procedure #6 gives general preference to the use of field-measured BAFs over laboratory-measured BCFs and requires FCMs to be used with BCF measurements for predicting BAFs. Guidance for deriving BAFs using Procedure #6 is provided in Section 5.6.4.

3. Determining whether or not biomagnification occurs for inorganic and organometallic chemicals requires chemical-specific data on measured concentrations of the chemical in aquatic organisms and their prey. Concentrations in aquatic organisms that increase substantially at successive trophic levels of a food web suggest that biomagnification is

occurring. Concentrations in aquatic organisms that remain about the same or decrease at successive trophic levels of a food web suggest that biomagnification is not occurring. When comparing tissue concentrations for assessing biomagnification, care should be taken to ensure that the aquatic organisms chosen actually represent functional predator-prey relationships and that all major prey species are considered in the comparisons.

5.6.2 Bioavailability

The chemical-specific nature of inorganic and organometallic bioavailability is likely due in part to chemical-specific differences in several factors which affect bioavailability and bioaccumulation. These factors include differences in the mechanisms for chemical uptake by aquatic organisms (e.g., passive diffusion, facilitated transport, active transport), differences in sorption affinities to biotic and abiotic ligands, and differences in chemical speciation in water. Some inorganic and organometallic chemicals exist in multiple forms and valence states in aquatic ecosystems that can differ in their bioavailability to aquatic organisms and undergo conversions between forms. For example, selenium can exist in various forms in aquatic ecosystems, including inorganic selenite($^{+4}$) and selenate($^{+6}$) oxyanions, elemental selenium (^{0}) under reducing conditions (primarily in sediments), and organoselenium compounds of selenide ($^{-2}$). Dominant forms of mercury in natural, oxic waters include inorganic ($^{+2}$) mercury compounds and methylmercury; the latter is generally considered to be substantially more bioavailable than inorganic mercury compounds to higher trophic level organisms. Although a generic analogue to the "freely dissolved" conversion for nonionic organic chemicals does not presently exist for inorganic and organometallic chemicals as a whole, the occurrence and bioavailability of different forms of these chemicals should be carefully considered when deriving national BAFs.

1. If data indicate that: (1) a particular form (or multiple forms) of the chemical of concern largely governs its bioavailability to target aquatic organisms, and (2) BAFs are more reliable when derived using the bioavailable form(s) compared with using other form(s) of the chemical of concern, then BAFs and BCFs should be based on the appropriate bioavailable form(s).

2. Because different forms of many inorganic and organometallic chemicals may interconvert once released to the aquatic environment, regulatory and mass balance considerations typically require an accounting of the total concentration in water. In these cases, sufficient data should be available to enable conversion between total concentrations and the other (presumably more bioavailable) forms in water.

5.6.3 Deriving BAFs Using Procedure #5

This section contains guidance for calculating national BAFs for inorganic and organometallic chemicals using Procedure #5 as shown in Figure 5-1. The types of inorganic and organometallic chemicals for which Procedure #5 is appropriate are those that are not likely to biomagnify in aquatic food webs (see Section 5.1 above). In Procedure #5, two methods are available to derive the national BAF for a given trophic level:

- using a BAF from an acceptable field study (i.e., field-measured BAF), or
- predicting a BAF from an acceptable laboratory-measured BCF.

Individual BAFs should be determined from field-measured BAFs or laboratory-measured BCFs according to the following guidelines.

5.6.3.1 Determining Field-Measured BAFs

1. Except where noted below, field-measured BAFs should be determined using the guidance provided in Section 5.4.3.1(A) of Procedure #1.

2. As described previously, conversion of field-measured BAFs to baseline BAF_{ℓ}^{fd}s based on lipid-normalized and freely-dissolved concentrations does not apply for inorganic and organometallic chemicals. Therefore, the guidance and equations provided in Procedure #1 which pertain to converting field-measured BAFs to baseline BAF_{ℓ}^{fd}s and subsequently to national BAFs do not generally apply to inorganic chemicals. As discussed in Section 5.6.2 above, an analogous procedure in concept might be required for converting total BAFs to BAFs based on the most bioavailable form(s) for some inorganic and organometallic chemicals of concern. Such procedures should be applied on a chemical-specific basis.

3. BAFs should be expressed on a wet-weight basis; BAFs reported on a dry-weight basis can be used only if they are converted to a wet-weight basis using a conversion factor that is measured or reliably estimated for the tissue used in the determination of the BAF.

4. BAFs should be based on concentrations in the edible tissue(s) of the biota unless it is demonstrated that whole-body BAFs are similar to edible tissue BAFs. For some finfish and shellfish species, whole body is considered to be the edible tissue.

5. The concentrations of an inorganic or organometallic chemical in a bioaccumulation study should be greater than normal background levels and greater than levels required for normal nutrition of the test species if the chemical is a micronutrient, but below levels that adversely affect the species. Bioaccumulation of an inorganic or organometallic chemical that is essential to the nutrition of aquatic organisms might be overestimated if concentrations are at or below normal background levels due to selective accumulation by the organisms to meet their nutritional requirements.

5.6.3.2 Determining Laboratory-Measured BCFs

1. Except where noted below, BAFs should be predicted from laboratory-measured BCFs using the guidance provided in Section 5.4.3.1(c) of Procedure #1.

2. As described previously, conversion of laboratory-measured BCFs to baseline BCF_{ℓ}^{fd}s based on lipid-normalized and freely dissolved concentrations does not apply for inorganic and organometallic chemicals. Therefore, the guidance and equations provided in Procedure #1 which pertain to converting laboratory-measured BCFs to baseline BCF_{ℓ}^{fd}s and subsequently to national BCFs do not generally apply to inorganic and organometallic chemicals. As discussed in Section 5.6.2 above, an analogous procedure in concept might be required for converting total BCFs to BCFs based on the most bioavailable form(s) of some inorganic and organometallic chemicals of concern. Such procedures should be applied on a chemical-specific basis. In addition, the use of FCMs with BCFs does not apply to chemicals applicable to Procedure #5.

3. BCFs should be expressed on a wet-weight basis; BCFs reported on a dry-weight basis can be used only if they are converted to a wet-weight basis using a conversion factor that is measured or reliably estimated for the tissue used in the determination of the BCF.

4. BCFs should be based on concentrations in the edible tissue(s) of the biota unless it is demonstrated that whole-body BCFs are similar to edible tissue BCFs. For some finfish and shellfish species, whole body is considered to be the edible tissue.

5. The concentrations of an inorganic or organometallic chemical in a bioconcentration test should be greater than normal background levels and greater than levels required for normal nutrition of the test species if the chemical is a micronutrient, but below levels that adversely affect the species. Bioaccumulation of an inorganic or organometallic chemical that is essential to the nutrition of aquatic organisms might be overestimated if concentrations are at or below normal background levels due to selective accumulation by the organisms to meet their nutritional requirements.

5.6.3.3 Determining the National BAFs

After calculating individual BAFs using as many of the methods in Procedure #5 as possible, the next step is to determine national BAFs for each trophic level from the individual BAFs. The national BAFs will be used to determine the national 304(a) criteria. The national BAFs should be determined from the individual BAFs by considering the data preference hierarchy defined for Procedure #5 and uncertainty in the data. The data preference hierarchy for Procedure #5 is:

1. a BAF from an acceptable field-measured BAF or predicted from an acceptable laboratory-measured BCF.

Since bioaccumulation via dietary uptake and subsequent biomagnification are not of concern for chemicals subject to Procedure #5, field-measured BAFs and laboratory-measured

BCFs are considered equally in determining the national BAFs. The national BAFs should be selected for each trophic level using the following steps and guidelines.

1. **Calculate Species-Mean BAFs.** For each BAF method where more than one acceptable field-measured BAF (or a BAF predicted from a BCF) is available for a given species, calculate the species-mean BAF as the geometric mean of all acceptable individual measured or BCF-predicted BAFs. When calculating species-mean BAFs, individual measured or BCF-predicted BAFs should be reviewed carefully to assess uncertainties in the BAF values. Highly uncertain BAFs should not be used. Large differences in individual BAFs for a given species (e.g., greater than a factor of 10) should be investigated further and in such cases, some or all of the BAFs for a given species might not be used. Additional discussion on evaluating the acceptability of BAF and BCF values is provided in the Bioaccumulation TSD.

2. **Calculate Trophic-Level-Mean BAFs.** For each BAF method where more than one acceptable species-mean BAF is available within a given trophic level, calculate the trophic-level-mean BAF as the geometric mean of acceptable species-mean BAFs in that trophic level. Trophic-level-mean BAFs should be calculated for trophic levels two, three and four because available data on U.S. consumers of fish and shellfish indicate significant consumption of organisms in these trophic levels.

3. **Select a Final National BAF for Each Trophic Level.** For each trophic level, select the final national BAF using best professional judgment by considering: (1) the data preference hierarchy in Procedure #5, and (2) the relative uncertainties among trophic level-mean BAFs derived using different methods.

    a. As discussed above, field-measured BAFs and laboratory-measured BCFs are considered equally desirable for deriving a final national BAF using Procedure #5. If a trophic-level-mean BAF is available from both a field-measured BAF and a laboratory-measured BCF, the final national BAF should be selected using the trophic-level-mean BAF with the least overall uncertainty.

    b. The above steps should be performed for each trophic level until a national BAF is selected for trophic levels two, three, and four.

5.6.4 Deriving BAFs Using Procedure #6

This section contains guidance for calculating national BAFs for inorganic and organometallic chemicals using Procedure #6 as shown in Figure 5-1. The types of inorganic and organometallic chemicals for which Procedure #6 is appropriate are those that are considered likely to biomagnify in aquatic food webs (see Section 5.6.1 above). Methylmercury is an example of an organometallic chemical to which Procedure #6 applies. In Procedure #6, two methods are available to derive the national BAF:

- using a BAF from an acceptable field study (i.e., field-measured BAF), or

- predicting a BAF from an acceptable laboratory-measured BCF and a FCM.

Individual BAFs should be determined from field-measured BAFs or laboratory-measured BCFs and FCMs according to the following guidelines.

5.6.4.1 Determining Field-Measured BAFs

1. Field-measured BAFs should be determined using the guidance provided in Section 5.6.3.1 of Procedure #5.

5.6.4.2 Determining Laboratory-Measured BCFs

1. Except where noted below, BAFs should be predicted from laboratory-measured BCFs using the guidance provided in Section 5.6.3.2 of Procedure #5.

2. Because biomagnification is of concern for chemicals applicable to Procedure #6, BAFs should be predicted from laboratory-measured BCF using FCMs. Currently, there are no generic models from which to predict FCMs for inorganic or organometallic chemicals. Therefore, FCMs should be determined using field data as described in the section entitled: "Field-Derived FCMs" in Section 5.4.3.1(c) of Procedure #1. Unlike nonionic organic chemicals, field-derived FCMs for inorganic and organometallic chemicals are not based on lipid-normalized concentrations in tissues. For calculating FCMs for inorganic and organometallic chemicals, concentrations in tissues should be based on the consistent use of either wet-weight or dry-weight concentrations in edible tissues. FCMs should be derived for trophic levels two, three, and four.

5.6.4.3 Determining the National BAF

After calculating individual BAFs using as many of the methods in Procedure #6 as possible, the next step is to determine national BAFs for each trophic level from the individual BAFs. The national BAFs will be used to determine the national 304(a) criteria. The national BAFs should be determined from the individual BAFs by considering the data preference hierarchy defined for Procedure #6 and uncertainty in the data. The data preference hierarchy for Procedure #6 is (in order of preference):

1. a BAF from an acceptable field-measured BAF, or
2. a predicted BAF from an acceptable laboratory-measured BCF and FCM.

This data preference hierarchy reflects EPA's preference for field-measured BAFs over BAFs predicted from a laboratory-measured BCF and FCM, because field-measured BAFs are direct measures of bioaccumulation and biomagnification in aquatic food webs. BAFs predicted from laboratory-measured BCFs and FCMs indirectly account for biomagnification through the use of the FCM. For each trophic level, the national BAFs should be determined using the following steps and guidelines.

1. **Calculate Species-Mean BAFs.** For each BAF method where more than one acceptable field-measured BAF or BAF predicted using a BCF and FCM is available, calculate a species-mean BAF according to the guidance described previously in Procedure #5.

2. **Calculate Trophic Level-Mean BAFs.** For each BAF method where more than one acceptable species-mean BAF is available within a given trophic level, calculate the trophic level-mean BAF according to guidance described previously in Procedure #5.

3. **Select a Final National BAF for Each Trophic Level.** For each trophic level, select the final national BAF using best professional judgment by considering: (1) the data preference hierarchy in Procedure #6, and (2) the relative uncertainties among trophic level-mean BAFs derived using different methods.

    a. When a trophic-level mean BAF is available using both methods for a given trophic level (i.e., a field-measured BAF and a BAF predicted from a BCF and FCM), the national BAF should usually be selected using the field-measured BAF which is the preferred BAF method in the data preference hierarchy in Procedure #6.

    b. If uncertainty in the trophic-level mean BAF derived using field-measured BAFs is considered to be substantially greater than a trophic-level mean BAF derived using a BCF and FCM, the national BAF for that trophic level should be selected from the second tier (BCF · FCM) method.

    c. The above steps should be performed for each trophic level until a national BAF is selected for trophic levels two, three, and four.

5.7 REFERENCES

ASTM (American Society of Testing and Materials). 1999. Standard practice for conducting bioconcentration tests with fishes and saltwater bivalve molluscs. Designation E 1022 - 94. In: *Annual Book of ASTM standards*. Volume 11.05. Pp. 333-350.

Barron, M.G. 1990. Bioconcentration: Will water-borne organic chemicals accumulate in aquatic animals? *Environ. Sci. Technol.* 24:1612-1618.

Burkhard, L.P. and M.T. Lukasewycz. 2000. Some bioaccumulation factors and biota-sediment accumulation factors for polycyclic aromatic hydrocarbons in lake trout. *Environ. Toxicol. Chem.* 19:1427-1429.

Carr, K.H., G.T. Coyle and R.A. Kimerle. 1997. Bioconcentration of [^{14}C]butyl benzyl phthalate in bluegill sunfish (*Lepomis Macrochirus*). *Environ. Toxicol. Chem.* 16:2200-2203.

Connell, D.W. 1988. Bioaccumulation behavior of persistent organic chemicals with aquatic organisms. *Rev. Environ. Contam. Toxicol.* 101:117-159.

Connolly, J.P. and C.G. Pedersen. 1988. A thermodynamic-based evaluation of organic chemical accumulation in aquatic organisms. *Environ. Sci. Technol.* 22:99-103.

Cook, P.M. and L.P. Burkhard. 1998. Development of bioaccumulation factors for protection of fish and wildlife in the Great Lakes. In: *National Sediment Bioaccumulation Conference Proceedings*. U.S. Environmental Protection Agency, Office of Water. Washington, DC. EPA 823-R-002.

de Wolf, W., J.H.M. de Bruijn, W. Seinen and J.L.M. Hermans. 1992. Influence of biotransformation on the relationship between bioconcentration factors and octanol-water partition coefficients. *Environ. Sci. Technol.* 26:1197-1201.

Fisk, A.T., R.J. Norstrom, C.C. Cymbalisty and D.C.B. Muir. 1998. Dietary accumulation and depuration of hydrophobic organochlorines: Bioaccumulation parameters and their relationship with the octanol/water partition coefficient. *Environ. Toxicol. Chem.* 17: 951-961.

Gobas, F.A.P.C., J.R. McCorquodale and G.D. Haffner. 1993. Intestinal absorption and biomagnification of organochlorines. *Environ. Toxicol. Chem.* 12:567-576.

Gobas, F.A.P.C. 1993. A model for predicting the bioaccumulation of hydrophobic organic chemicals in aquatic food-webs: application to Lake Ontario. *Ecol. Mod.* 69:1-17

Hudson, R.J.M., A.S. Gherini, C.J. Watras and D.B. Porcella. 1994. Modeling the biogeochemical cycle of mercury in lakes: the Mercury Cycling Model (MCM) and its application to the MTL Study Lakes, In: C.J. Watras and J.W. Huckabee (eds.), *Mercury Pollution: Integration and Synthesis.* Lewis Publishers. Boca Raton, FL. Pp. 473-523.

Isnard, P. and S. Lambert. 1988. Estimating bioconcentration partition coefficients and aqueous solubility. *Chemosphere* 17:21-34.

Jafvert, C.T. 1990. Sorption of organic acid compounds to sediments: initial model development. *Environ. Toxicol. Chem.* 9:1259-1268.

Jafvert, C.T., J.C. Westall, E. Grieder and R.P. Schwarzenbach. 1990. Distribution of hydrophobic ionogenic organic compounds between octanol and water: Organic acids. *Environ. Sci. Technol*. 24:1795-1803.

James, M.O. 1989. Biotransformation and disposition of PAH in aquatic invertebrates, In: U. Varanasi (ed.). *Metabolism of Polycyclic Aromatic Hydrocarbons in the Aquatic Environment*. CRC Press, Inc. Boca Raton, FL. Pp. 69-92.

Mackay, D. 1982. Correlation of bioconcentration factors. *Environ. Sci. Technol.* 16:274-278.

Miranda, C.L., M.C. Henderson, and D.R. Buhler. 1998. Evaluation of chemicals as inhibitors of trout cytochrome p450s. *Toxicol. Appl. Pharmacol*. 148:327-244.

Niimi, A.J. 1985. Use of laboratory studies in assessing the behavior of contaminants in fish inhabiting natural ecosystems. *Wat. Poll. Res. J. Can.* 20:79-88.

Oliver, B.G. and A.J. Niimi. 1983. Bioconcentration of chlorobenzenes from water by rainbow trout: Correlations with partition coefficients and environmental residues. *Environ. Sci. Technol.* 17:287-291.

Oliver, B.G. and A.J. Niimi. 1988. Trophodynamic analysis of polychlorinated biphenyl congeners and other chlorinated hydrocarbons in the Lake Ontario ecosystem. *Environ. Sci. Technol*. 22:388-397.

Randall, R.C., H. Lee II, R.J. Ozretich, J.L. Lake and R.J. Pruell. 1991. Evaluation of Selected Lipid Methods for Normalizing Pollutant Bioaccumulation. *Environ. Toxicol. Chem.* 10: 1431-1436.

Randall, R.C., D.R. Young, H. Lee, and S.F. Echols. 1998. Lipid methodology and pollutant normalization relationships for neutral nonpolar organic pollutants. *Environ. Toxicol. Chem*. 17:788-791.

Russell, R.W., F.A.P.C. Gobas, and G.D. Haffner. 1999. Role of chemical and ecological factors in trophic transfer of organic chemicals in aquatic food webs. *Environ. Toxicol. Chem*. 18:1250-1257.

Schwarzenbach, R.P., P.M. Gschwend, and D.M. Imboden. 1993. *Environmental Organic Chemistry*. John Wiley and Sons, Inc. New York, NY.

Spacie, L.L. 1994. Interactions of organic pollutants with inorganic solid phases: are they important to bioavailability? In: *Bioavailability: Physical, Chemical and Biological Interactions.* Hamelink, J.L., Landrum, P.F., Bergman, H.L., and W.H. Benson (eds.). Proceedings of the Thirteenth Pellston Workshop, Pellston, MI. August 17-22, 1992. SETAC Special Publication Series. CRC Press, Inc. Boca Raton, FL. Pp. 73-82.

Suffet, I.H., C.T. Jafvert, J. Kukkonen, M.R. Servos, A. Spacie, L.L. Williams, and J.A. Noblet. 1994. Synopsis of discussion sessions: influence of particulate and dissolved material on the bioavailability of organic compounds, In: *Bioavailability: Physical, Chemical and Biological Interactions.* Hamelink, J.L., Landrum, P.F., Bergman, H.L., and W.H. Benson (Eds.). Proceedings of the Thirteenth Pellston Workshop, Pellston, MI. August 17-22, 1992. SETAC Special Publication Series. CRC Press, Inc. Boca Raton, FL. Pp. 93-108.

Swackhamer, D.L. and R.A. Hites. 1988. Occurrence and bioaccumulation of organochlorine compounds in fishes from Siskiwit Lake, Isle Royale, Lake Superior. *Environ. Sci. Technol.* 22:543-548.

Thomann, R.V. 1989. Bioaccumulation model of organic chemical distribution in aquatic food chains. *Environ. Sci. Technol*. 23:699-707.

USEPA (U.S. Environmental Protection Agency). 1980. Appendix C–Guidelines and methodology used in the preparation of health effect assessment chapters of the consent decree water criteria documents. *Federal Register* 45:79347-79357. November 28.

USEPA (U.S. Environmental Protection Agency). 1991. *Technical Support Document for Water Quality-Based Toxics Control.* Office of Water. Washington, DC. EPA/505/2-90/001.

USEPA (U.S. Environmental Protection Agency). 1993. Assessment and control of bioconcentratable contaminants in surface water. *Federal Register* 56:13150.

USEPA (U.S. Environmental Protection Agency). 1995a. Final water quality guidance for the Great Lakes system; Final Rule. *Federal Register* 60:15366-15425. March 23.

USEPA (U.S. Environmental Protection Agency). 1995b. *Great Lakes Water Quality Initiative Technical Support Document for the Procedure to Determine Bioaccumulation Factors.* Office of Water. Washington, DC. EPA/820/B-95/005.

USEPA (U.S. Environmental Protection Agency). 1996. *Ecological Effects Test Guidelines. OPPTS 850.1730 Fish BCF. Public Draft.* Office of Prevention, Pesticides and Toxic Substances. Washington, DC. EPA/712/C-96/129. April.

USEPA (U.S. Environmental Protection Agency). 1997. Revisions to the polychlorinated biphenyl criteria for human health and wildlife for the water quality guidance for the Great Lakes system; Final Rule. *Federal Register* 62:11723-11731. March 12.

USEPA (U.S. Environmental Protection Agency). 2000a. *Trophic Level and Exposure Analyses for Selected Piscivorous Birds and Mammals. Volume I: Analyses of Species for the Great Lakes. Draft*. Office of Water. Washington, DC. August.

USEPA (U.S. Environmental Protection Agency). 2000b. *Trophic Level and Exposure Analyses for Selected Piscivorous Birds and Mammals. Volume II: Analyses of Species in the Conterminous United States. Draft.* Office of Water. Washington, DC. August.

USEPA (U.S. Environmental Protection Agency). 2000c. *Trophic Level and Exposure Analyses for Selected Piscivorous Birds and Mammals. Volume III: Appendices. Draft*. Office of Water. Washington, DC. August.

USEPA (U.S. Environmental Protection Agency). 2000d. *Technical Basis for the Derivation of Equilibrium Partitioning Sediment Guidelines (ESGs) for the Protection of Benthic Organisms: Nonionic Organics.* Office of Science and Technology, Office of Research and Development. Washington, DC. June Draft.

Veith, G.D., D.F.L. DeFoe and B.V. Bergstedt. 1979. Measuring and estimating the bioconcentration factor in fish. *J. Fish. Res. Board Can.* 36:1040-1045.

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October 31, 2001

Western States Petroleum Association (WSPA)
1115 11th Street, Suite 150
Sacramento, CA 95814

Attention: Kevin Buchan

Subject: Comments on proposed tentative order renewing
NPDES Permit CA0005789
NPDES SUPPORT PERMIT CA0005789
CONTRACT NO. RB 0101-12
FSI 014068

Dear Mr. Buchan:

Flow Science was retained by the Western States Petroleum Association (WSPA) in October 2001 to review information related to discharge Waste 001, which is addressed by a tentative order issued to renew NPDES permit CA0005789. Specifically, Flow Science was asked to comment upon Finding 22, which addresses the issues of dilution and assimilative capacity from the Equilon Martinez diffuser, through which Waste 001 is discharged to Carquinez Strait. This analysis was conducted by Susan C. Paulsen, Ph.D., a Senior Scientist at Flow Science, and reviewed by E. John List, Ph.D., P.E., Principal Consultant. Dr. Paulsen's qualifications are summarized in Attachment A.

Executive summary

The premise of withholding a dilution credit based upon an "assimilative capacity," or lack thereof, makes little sense when detailed information about the Equilon Martinez Waste 001 is reviewed.

Four field studies of dilution and two model studies of near-field dilution studies have shown that rapid near-field mixing is achieved by the Equilon Martinez diffuser. Field studies have been conducted under a variety of conditions, including "worst case" receiving water conditions and a range of effluent flow rates. Both the field and model studies show that average dilution at the edge of the mixing zone is about 30:1 or greater. Thus, it would be appropriate to grant a 30:1 dilution (rather than a 10:1 dilution) on the basis of the measured and modeled diffuser performance.

Because of the strongly tidal nature of flow in the estuary and past the diffuser location, tidal flushing is significant, and far-field, long-term average dilution exceeds

3000:1. Thus, there is little opportunity for constituents discharged from the Martinez Equilon diffuser to "build up" within the estuary. Even for the bioaccumulative pollutants of dioxin, PCBs, 4,4-DDE, and dieldrin, there is no evidence that discharges from the Martinez Equilon diffuser are in any way responsible for elevated concentrations in receiving waters, sediments, or biota. Similarly, there is no evidence supporting the hypothesis that enforcing the effluent limits proposed in the tentative order for these constituents would result in any discernible decrease in concentrations of these constituents in receiving waters, sediments, or biota. Any decision to set effluent limits of these constituents as proposed in the tentative order cannot be justified on scientific mass balance principles. Finally, these arguments also lead to the conclusion that there is no scientific reason for denying a dilution credit for these pollutants. The basis for these statements is provided below.

Introduction

As stated in Finding 22 of the proposed order, Regional Board staff "has found that the assimilative capacity [of the receiving water] is highly variable due to the complex hydrology of the receiving water." Further, Board staff have referenced "uncertainty associated with the representative nature of the appropriate ambient background data to conclusively quantify the assimilative capacity of the receiving water [sic]." Thus, Finding 22 of the tentative order states that a "dilution credit is not included in calculating the final WQBEL" for bioaccumulative pollutants. As stated in Finding 42 of the tentative order, this decision is based upon the assumption that the receiving water lacks assimilative capacity. For non-bioaccumulative pollutants, a 10:1 dilution is granted.

Effluent limitations are developed in the tentative order for six bioaccumulative pollutants. Two of these (selenium and mercury) have been assigned interim mass-based and concentration-based effluent limitations, which will be in place until a TMDL is established for these pollutants. Four bioaccumulative pollutants (dioxins and furans, PCBs, 4,4-DDE, and dieldrin) are assigned effluent limits as specified in the effluent limitations section of the tentative order; effluent limits for these four constituents do not include or consider dilution from the diffuser.

In preparing these comments, Flow Science has reviewed receiving water data, effluent data, and previous studies related to discharge from the Equilon Martinez diffuser. Flow Science has also conducted additional analysis and calculations. These comments are divided into three sections, which address near-field dilution, far-field dilution, and the issue of assimilative capacity of the receiving water with respect to the bioaccumulative pollutants mentioned above.

When considering the impacts of effluent discharged from a diffuser into a receiving water body, it is important to consider both near-field and far-field dilution. Near-field dilution is the initial mixing between the effluent and the receiving water that occurs near the point of discharge. Far-field dilution of a discharge is the dilution that occurs at some distance from the discharge location. For a continuous discharge (such as the discharge from the Equilon diffuser), a steady-state concentration of discharged effluent (representing the balance between the supply at the discharge location and the removal of the discharge from the estuary via flushing) will develop within the estuary over time. It is these steady-state, long-term concentrations of the discharge that must be used in assessing the impact of the discharge on an estuary outside of the near-field dilution zone.

Evaluation of near-field dilution

Diffusers are used to promote rapid mixing of a discharge with the receiving water. This rapid initial mixing is achieved by the entrainment of ambient fluid, and the dilution achieved from a diffuser is a function of the diffuser design, the effluent characteristics, and the characteristics of the receiving water. In the case of the Equilon Martinez diffuser, initial mixing is caused both by the momentum of the effluent as it exits the diffuser ports and by the relative buoyancy of the effluent with respect to the receiving water.

Treated wastewater from the Martinez Refinery is pumped through a 24-inch diameter, half-mile long outfall pipe. The outfall terminates in a 60-foot diffuser located beneath the east wharf of the marine terminal. The diffuser consists of 20 ports (3-inch holes in the outfall pipe) spaced on 3-foot centers; ports are located on the downstream (southwest) side of the pipe. The diffuser is located approximately 20 feet below mean low lower water (MLLW) and is attached to pilings beneath the wharf. Currently, effluent is discharged continuously at an average flow rate of about 5.7 mgd; the tentative permit is written for an average annual discharge of 6.7 mgd. The discharged effluent is buoyant with respect to the receiving water. The average monthly temperature of the discharge generally ranges from about 75°F to about 90°F[1]. The measured conductivity of the discharge ranges from 2,290 μmhos/cm to 6,730 μmhos/cm (or representing a salinity of about 1.4 ppt – 4.0 ppt)[2]. Both temperature and salinity vary seasonally, with warmer effluent temperatures and higher salinities in the summer and fall months.

Conditions in the receiving water also vary seasonally, with high salinity water (up to about 20 ppt salinity) present at Martinez during dry (i.e., low Delta freshwater

[1] Dan Glaze, personal communication, October 29, 2001.
[2] Dan Glaze, personal communication, October 18, 2001.

outflow) conditions. During times of high freshwater outflow from the Delta, salinity at Martinez drops. Near-surface water temperature is measured by DWR at Martinez and varies seasonally from around 45°F to about 70°F[3]. Even when freshwater conditions are present in the receiving water near the Martinez Equilon diffuser, the effluent has a positive (upward) buoyancy, promoting buoyant mixing of the Waste 001 discharge.

Field Studies

Four detailed field studies of the near-field dilution attained near the Equilon Martinez diffuser have been conducted. These studies have used tracers to measure the initial dilution of effluent discharged from the diffuser under a wide range of tidal conditions and receiving water conditions. Flow Science has reviewed each of these studies and conducted new modeling analyses as appropriate to determine the effects of the effluent flow rates specified in the tentative order.

The first field study of dilution from the Martinez diffuser was conducted by Water Resources Engineers (WRE) in 1968[4]. Two field tests evaluated the discharge of wastes pumped during ebb tide at 10,000 gpm. (Note that this discharge rate is equivalent to 14.4 mgd, more than double the flow rate of 6.7 mgd in the tentative permit.) A third field test was used to evaluate a reduced discharge rate, and two additional tests were used to evaluate near-field dilution during a flood tide. Rhodamine B, a fluorescing liquid dye, was used as the tracer. Current measurements were also collected during a current study both with tankers docked at both the east and west stations of the wharf and with no tankers present at the wharf. As detailed in the study report, currents beneath the wharf were characterized by "constant eddying, lacking a well-structured or strong flow pattern…current velocity and direction at each station and depth was [sic] constantly changing in a somewhat random manner."[5] Current velocities under the wharf were approximately one-half to one-quarter the velocities in the main channel adjacent to the wharf (with higher velocities when tankers were present at the wharf). WRE also noted that the presence of pilings beneath the wharf increases the dilution of the discharge over that which would be achieved in open waters. Five dye tracer runs were performed during the study, and WRE concluded that average dilution at the edge of the rising waste plume was between 22:1 and 29:1, with greater near-field dilutions possible during stronger ebb tides, during flood tides, and/or with reduced discharge flow rates. Note that the temperature and salinity of the effluent and the receiving water were not reported.

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[3] California Data Exchange Center (CDEC), data for Martinez station, accessed at http://cdec.water.ca.gov/ on October 29, 2001.
[4] Water Resources Engineers, Inc. A Report to Shell Oil Co., Martinez Refinery on Waste Effluent Diffuser Evaluation. October 1968.
[5] Ibid., at p. 8.

A second dilution field study was performed by the Shell Development Company in 1969[6]. Four field tests were performed as part of this study, which utilized a radioactive tracer (radio-labeled sodium bromide, labeled with bromine-82, or ^{82}Br). Two field tests were conducted during ebb tide conditions and two during flood tide conditions. The field tracer tests were conducted under a variety of receiving water conditions, ranging from high freshwater flow conditions (May 1969) to more saline receiving water conditions in August 1969 and later. In this study, as in the WRE (1968) study, the presence of a docked vessel at the wharf was observed to increase velocities in the receiving water near the diffuser, and currents were observed to be highly variable beneath the wharf. Results of these field studies are summarized in Table 1, below.

Table 1. Summary of results from dye studies conducted in 1969 and reported in Shell (1970).

	Test 1	Test 2	Test 3	Test 4
Test date	5/14/1969	8/28/1969	9/27/1969	10/24/1969
Effluent flow rate [mgd]	11.4-18.7	12.7-13.2	13.2	15.0-15.3
Tide condition	Flood	Flood	Ebb	Ebb
Ships/barges present?	Yes (last 2 hours of test)	NR	NR	NR
Effluent temperature [°F]	NR	85	NR	NR
Effluent chloride concentration [ppt]	NR	0.2	NR	NR
Receiving water temperature [°F]	NR	66	NR	NR
Receiving water chloride concentration [ppt]	0.5	6	NR	NR
Receiving water velocity [m/s][a]	0.49-0.66	0.15-0.21	0.23-0.52	0.09-0.30
Observed weighted average dilution	82-110[b]	71-93[b]	58-81[c]	39-64[c]

[a] Note that the location of this measurement varied, and velocities near the diffuser may have been significantly lower.
[b] At a location 236 feet NE of the diffuser centerline (i.e., downstream during flood tide).
[c] At a location 265 feet SW of the diffuser centerline (i.e., downstream during ebb tide).
NR: not reported

[6] Siegel, H., A. Telfer, and E.L. Bastin. A tracer study of initial dilution of waste water from a subsurface diffuser in a tidal estuary: Evaluation of the Martinez Refinery diffuser. Shell Development Company Technical Progress Report No. 37-70, Project No. 50700.

The third field dilution study was conducted by EA Engineering, Science, and Technology, Inc., in November 1985[7]. Dye studies were performed using Rhodamine dye during two ebb tides and one flood tide. Results of dye studies were compared to model results (described in greater detail below) to verify modeling. By design, the dye studies were conducted under conditions defined by EA as "most conservative," i.e., low river outflow and high receiving water salinity. EA carried out an additional current study on June 17, 1986, to measure the influence of wharf pilings and the presence of ships docked at the wharf on velocities in the vicinity of the diffuser. EA found that the combination of pilings and ships caused a significant reduction in velocity compared to predicted open-water velocities, consist with findings in the earlier reports. The EA report did not examine changes in velocity beneath the wharf due solely to the presence or absence of ships. Results of the dye studies are shown in Table 2 below. From these results, EA concluded that "minimum dilution (i.e., centroid dilution when the plume surfaced) average 39:1 on ebb tide and 35:1 on flood."[8]

Test 2. Summary of results from dye studies conducted in 1985 and reported in EA (1986).

	Test 1	**Test 2**	**Test 3**
Test date	11/8/1995	11/9/1995	11/9/1995
Effluent flow rate [mgd]	NR, but likely 4.1 - 4.3 mgd		
Tide condition	Ebb	Flood	Ebb
Ships/barges present?	Yes, during at least some portion of the tests		
Effluent temperature [°F]	70[a]	70[a]	70[a]
Effluent salinity [ppt]	1.5[a]	1.5[a]	1.5[a]
Receiving water temperature [°F]	61.3	60.1	58.8
Receiving water salinity [ppt]	19.0	17.7	19.9
Receiving water velocity [m/s]	NR	NR	NR
Minimum observed dilution at any depth in plume and at surface	23.0 - 69.9[b] 37 at surface	22.1 - >200[c] 35 at surface	41.3 – 143[d] >41 at surface

[a] Data are given for modeling study and were selected to match conditions during the field dye study. Measurements made during the field dye study are not reported.

[b] From measurements of dye concentration with depth at distances 25 to 200 feet downstream of the diffuser along the plume centerline; note that only a single value of 23.0:1 was measured at 5.9 m depth 25 feet from the diffuser, i.e., within the zone of initial dilution. All other values exceeded 37:1.

[c] From measurements made from 50 feet upstream of the diffuser to 175 feet downstream of the diffuser along the centerline of the plume. Again, only a single value of 22.1:1 was measured at 6.5 m depth 25 upstream of the diffuser, i.e., within the initial zone of dilution. All other values exceeded 30.8:1.

[d] From measurements made at distances 25 to 200 feet downstream of the diffuser along the plume centerline.

NR: not reported

[7] EA Engineering, Science, and Technology, Inc. Final: Derivation of water quality-based toxicity effluent limits for the Shell Oil Martinez Manufacturing Complex. August 1986.

[8] Ibid., p. 17.

The fourth and most recent field tracer study was conducted by Brown and Caldwell in July 1987[9]. Rhodamine WT was injected into the effluent for several hours each day during the dye study, capturing a range of receiving water conditions during both flood and ebb tides. Receiving water temperatures ranged from 18.9°C to 19.9°C (66.0°F to 67.8°F), with strongest temperature stratification during peak ebb tides. Receiving water salinity varied significantly, from 12.6 ppt near the surface at peak flood to 19.7 ppt near the bottom during slack before ebb. Net Delta Outflow (NDO, a measure of the freshwater flow from the estuary) was estimated to be 3,050 cfs. Current measurements made during the study confirmed that wharf pilings and tankers docked at the wharf affected current speeds beneath the wharf, with measured currents ranging from 17% to 42% of predicted maximum channel currents. Although temperature and salinity of the effluent are not reported, the effluent was strongly buoyant, and dye concentrations were measured primarily at the surface (i.e., height of rise of the plume). The effluent flow rate during the dye study was held constant at 2,800 gpm (4.0 mgd). Brown and Caldwell also provided the results of a statistical compilation of current measurements in the vicinity of the diffuser taken from July 23-26, 1987, that showed strongly tidal flow. These results showed that current velocities were less than 0.025 m/s only 2.8% of the time, and less than 0.05 m/s only 5.4% of the time.

Dye measurements made by Brown and Caldwell (1987) in general showed rapid dilution near the diffuser. Results are summarized in Table 3, below. Instantaneous measurements of dye at the surface showed small areas of dilution as low as 16.3:1, and dilutions less than 20:1 were observed only within 15 lateral feet of the diffuser (i.e., within the zone of initial dilution). These dye studies showed time-averaged near-field dilutions (i.e., at the edge of the zone of initial dilution) nearer to 30:1. The “blobby” or “puffy” nature of the plume is also clearly shown in vertical dye concentration profiles, which show variations in surface dye concentrations of up to eight-fold over only a few minutes (e.g., variation from 2 ppb to 15 ppb just below the surface in one vertical profile). The plume likely experiences very localized, short-lived “puffs” of higher concentration effluent due to the erratic nature of the velocity of the receiving water in the vicinity of the diffuser. Brown and Caldwell took care to observe dye concentrations during slack tide conditions, and their results show that even during slack tide, ambient turbulence and near-field mixing in the vicinity of the diffuser is significant.

[9] Brown and Caldwell. Water quality and dye dilution studies, Martinez Manufacturing Complex, Shell Oil Company. Ocrober 1987.

Table 3. Summary of results from dye studies conducted in July 1987 and reported in Brown and Caldwell (1987).

	Period 1	Period 2	Period 3	Period 4	Period 5	Period 6	Period 7
Test date Test time	7/24 1148-1204	7/24 1533-1546	7/24 1612-1620	7/24 1620-1632	7/25 1027-1031	7/25 1203-1223	7/27 1044-1050
Effluent flow rate [mgd]	4.3	4.3	4.3	4.3	4.3	4.3	4.3
Tide condition	Flood	Near slack	Slack	Slack → ebb	Slack → flood	Flood	Slack → flood
Receiving water temperature [°F]	18.9°C - 19.9°C (66.0°F – 67.8°F) on 7/23/87						
Receiving water salinity [ppt]	12.6 ppt – 19.7 ppt Stratified						
Receiving water velocity [m/s][a]	0.012 to NE	0.06 to NE	0 Erratic	0-0.02 Erratic	0.15 to N	Erratic	NR
Observed minimum dilution at surface	16.3	22.6	33.4	32.8	17.0	24.5	36.8
Approx. lateral distance from diffuser to peak concentration	19 ft	14 ft	64 ft	64 ft	14 ft	37 ft	62 ft
Observed average dilution across plume[b]	21	31	43	47	21	32	51

[a] Estimated from vector diagrams contained in figures in Brown and Caldwell (1987) report.
[b] Estimated from contour plots of surface dye concentrations contained in figures in Brown and Caldwell (1987) report. Estimates were made from average dye concentration across the plume at the location where the minimum surface dilution was observed.
[c] At a location 265 feet SW of the diffuser centerline (i.e., downstream during ebb tide).
NR: not reported

Diffuser Modeling Analysis

Modeling of near-field dilution is useful to estimate plume behavior under a variety of conditions. For example, modeling may be used to predict dilution for conditions different from those observed during field studies, or to examine the effects of operational changes. Numerical dilution modeling was first reported by EA Engineering,

Science, and Technology (1986). The original modeling by EA was conducted using the April 1984 version of the UDKHDEN model, a plume dilution model that simulates the near-field behavior of diffuser discharges. Conditions corresponding to those observed during the three dye studies conducted by EA (described above) were replicated in the model. EA found that the UDKHDEN model-predicted dilutions compared well to dye study results, particularly for the no-flow (i.e., zero velocity) condition. After comparison to field study results, EA used the model to predict dilution under "worst case" receiving water conditions, defined as 95th percentile most conservative case values (see EA, 1986). In all cases, EA found that the "minimum expected dilution for the Shell effluent at the edge of the ZID is approximately 33:1."[10] EA also found that UDKHDEN predictions for current speeds greater than 0.05 m/s produced dilutions higher than those observed at the same locations in the field dye studies.

Since 1986, when EA conducted modeling of the diffuser, the UDKHDEN model has been updated and improved and is now called the DKHW model[11]. In addition, the tentative permit has been written for an average effluent flow of 6.7 mgd, higher than the effluent flow modeled by EA (1986). Using the updated DKHW model, Flow Science modeled conditions identical to those modeled by EA (1986). Tabulated results of the dilution modeling conducted by EA (1986) and Flow Science (2001) are presented in Table 4 below. Four different cases were modeled, corresponding to four different receiving water conditions. Two ambient salinity and temperature profiles were modeled and are presented in Table 5; three different flow velocities were also modeled. The first two columns in Table 4 show model results for the four modeled cases for the same conditions. Model results agree well, confirming that the predictions of the DKHW model are consistent with the results of the field studies. In fact, the Flow Science (2001) modeling produces lower dilutions when ambient flow velocities are high (Case 3), in much better agreement with dye study results than the earlier EA (1986) modeling. Thus, the DKHW model seems to correct one of the flaws of the earlier UDKHDEN model, producing more reasonable near-field dilution results for non-stagnant flow conditions.

Flow Science also used the DKHW model to simulate increased average effluent flow rates to the level specified in the tentative NPDES permit; other modeled conditions remained the same. These results, shown in the fourth column of Table 4, demonstrate that the near-field dilution attained by the diffuser operating under increased effluent flow rates is consistent with the earlier results. At the tentative permit average annual flow rate of 6.7 mgd, a dilution of 29.6:1 or greater is expected at the edge of the near-field zone.

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[10] EA (1986), at p. 17.

[11] Frick, W.E., P.J.W. Roberts, L.R. Davis, J. Keyes, D.J. Baumgartner, and K.P. George. Dilution models for effluent discharges, 4th edition (Visual Plumes), draft. July 18, 2001.

Table 4. Results of numerical modeling of 95th percentile-most-conservative-case values. See EA (1986) for definition of most conservative case.			
Model parameter	**EA (1986) model results**	**Flow Science (2001) results for 1986 flows**	**Flow Science (2001) results for permit flows**
Diffuser characteristics			
Number of ports	20	20	20
Port diameter	3 in	3 in	3 in
Port spacing	3 ft	3 ft	3 ft
Port depth	20 ft	20 ft	20 ft
Model conditions: case 1			
Effluent flow rate	4.31 mgd	4.31 mgd	6.7 mgd
Effluent salinity	1.50 ppt	1.50 ppt	1.50 ppt
Effluent temperature	70°F	70°F	70°F
Ambient current	0 m/s	0 m/s	0 m/s
Ambient profile	Profile A	Profile A	Profile A
Model results: case 1			
Trapping depth	--	--	--
Dilution at trapping depth	--	--	--
Height of max. rise	water surface	water surface	water surface
Dilution at max. rise	31.7	30.0	29.6
Distance from diffuser of max. rise	19.1 ft	19.6 ft	28.8 ft
Model conditions: case 2			
Effluent flow rate	4.31 mgd	4.31 mgd	6.7 mgd
Effluent salinity	1.50 ppt	1.50 ppt	1.50 ppt
Effluent temperature	70°F	70°F	70°F
Ambient current	0.05 m/s	0.05 m/s	0.05 m/s
Ambient profile	Profile A	Profile A	Profile A
Model results: case 2			
Trapping depth	5.2 ft	6.9 ft	2.2 ft
Dilution at trapping depth	64.45	58.4	58.1
Depth of max. rise	1.0 ft	0.21 ft	water surface
Dilution at max. rise	78.1	81.1	62.6
Distance from diffuser of max. rise	33.3 ft	48.7 ft	42.7 ft

Model parameter	EA (1986) model results	Flow Science (2001) results for 1986 flows	Flow Science (2001) results for permit flows
Model conditions: case 3			
Effluent flow rate	4.31 mgd	4.31 mgd	6.7 mgd
Effluent salinity	1.50 ppt	1.50 ppt	1.50 ppt
Effluent temperature	70°F	70°F	70°F
Ambient current	0.10 m/s	0.10 m/s	0.10 m/s
Ambient profile	Profile A	Profile A	Profile A
Model results: case 3			
Trapping depth	14.2 ft	12.9 ft	12.7 ft
Dilution at trapping depth	102	58.9	48.4
Depth of max. rise	3.2 ft	10.8 ft	9.2 ft
Dilution at max. rise	118	72.4	64.2
Distance from diffuser of max. rise	49.9 ft	35.8 ft	46.5 ft
Model conditions: case 4			
Effluent flow rate	4.10 mgd	4.10 mgd	6.7 mgd
Effluent salinity	1.50 ppt	1.50 ppt	1.50 ppt
Effluent temperature	70°F	70°F	70°F
Ambient current	0 m/s	0 m/s	0 m/s
Ambient profile	Profile B	Profile B	Profile B
Model results: case 4			
Trapping depth	--	--	--
Dilution at trapping depth	--	--	--
Height of max. rise	water surface	water surface	water surface
Dilution at max. rise	32.5	31.3	30.0
Distance from diffuser of max. rise	18.4 ft	18.9 ft	28.4 ft

Table 5. Receiving water salinity and temperature profiles used in modeling (see Table 4).		
Water depth [m]	**Salinity [ppt]**	**Temperature [°C]**
Profile A		
0.00	19.56	14.78
0.50	19.59	14.79
2.13	20.63	14.82
3.96	20.62	14.88
6.20	20.68	14.82
Profile B		
0.00	17.50	8.00
1.52	17.50	8.00
2.13	17.30	7.67
2.74	17.93	6.67
3.35	17.23	6.21
3.96	17.26	6.21
4.57	17.39	6.22
5.18	17.52	6.26
5.79	17.34	6.96
6.10	17.34	6.96

In summary, the results of four separate field tracer studies and two near-field plume models all show that the minimum average dilution in the near-field of the discharge from the Equilon Martinez diffuser is approximately 30:1 or greater. These tracer and modeling studies span the range of expected conditions, including the range of expected effluent flows, effluent temperature and salinity, receiving water temperature and salinity, and tidal conditions. Dye study results were obtained both when ships or barges were present at the wharf and when they were not. Based upon the review of previous studies and data and additional modeling, Flow Science concludes that the appropriate near-field average dilution ratio is 30:1 or greater. As detailed below, this dilution ratio is applicable for both bioaccumulative and non-bioaccumulative pollutants.

Evaluation of far-field dilution

Because San Francisco Bay is a dynamic, tidally-driven, open system, flushing is far greater than in a closed (or nearly closed) system, such as the Great Lakes. On each tidal cycle, an average volume of approximately 1.3 million acre-feet (about 423 billion gallons) moves into and out of the San Francisco Bay estuary at the Golden Gate (SFEP,

1992[12]; Cohen, 2000[13]). This volume of water is approximately 24% of the total volume of water contained in the estuary (SFEP, 1992; Cohen, 2000).

While part of the volume of water that enters the Bay during the flood tide is made up of water that left the Bay on previous ebb tides, part of the water that enters the Bay is "new" ocean water. The "tidal exchange ratio," often called "R," is the ratio of new ocean water to the total volume of water that enters the Bay during a flood tide. Fischer et al. (1979) report the results of measurements of tidal exchange at the entrance to San Francisco Bay; see Attachment B. The average tidal range at the Golden Gate can be calculated from tidal measurements made at this location and is approximately 5.5 feet (see also Cohen, 2000). Thus, the average tidal exchange ratio at the mouth of the San Francisco Bay and the associated estuary is estimated to be about 0.3, or 30%. This means that approximately 390,000 acre-feet of "new" ocean water enter the estuary on each tidal cycle. Since there are two tidal cycles every 24.8 hours, approximately 755,000 acre-feet of "new" ocean water enter the estuary every day.

Extensive measurements have been made of flow velocities within Carquinez Strait. Data collected by the United States Geological Survey (USGS) at the west end of Carquinez Strait show that flow velocities within Carquinez Strait almost always exceed 0.5 m/s and routinely exceed 1 m/s during tidal cycles (Burau et al., 1993[14]). The strong tidal nature of flows in Carquinez Strait can also be seen by measurements of water surface elevation made by DWR at Martinez. The tidal excursion as measured at Martinez (near the Equilon discharge) generally ranges from about 3 feet to about 7 feet (data from CDEC, 2001[15]).

Flows in Carquinez Strait consist primarily of tidal flows and of freshwater flows that leave the Delta and enter San Francisco Bay via the Strait. Because tidal flows are much larger than freshwater flows at the western edge of the Delta and in Carquinez Strait, the net freshwater flow entering the Bay from the Delta cannot be measured directly. The net freshwater flow is instead calculated as the difference between water arriving to the Delta (via river flow and precipitation) and water removed within the Delta (via in-Delta use and exports/diversions). The average annual Net Delta Outflow

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[12] San Francisco Estuary Project, 1992. State of the Estuary Report: A Report on Conditions and Problems in the San Francisco Bay/Sacramento-San Joaquin Delta Estuary. San Francisco Estuary Institute, available at http://www.abag.ca.gov/bayarea/sfep/reports/soe.

[13] Cohen, A.N. 2000. An Introduction to the San Francisco Estuary. Third, Ed., Draft. Save the Bay, San Francisco Estuary Project, and San Francisco Estuary Institute.

[14] Burau, J.R., Simpson, M.R., Cheng, R.T. 1993. Tidal and residual currents measured by an acoustic doppler current profiler at the west end of Carquinez Strait, San Francisco Bay, California, March to November 1988. Water Resources Investigation Report 92-4064. United States Geological Survey, Sacramento, California.

[15] California Data Exchange Center (CDEC), http://cdec.water.ca.gov/, Station MRZ (Martinez), accessed on October 15, 2001.

ranges from 5,431 cfs to 60,179 cfs during the time period 1984-1999 (based on data from IEP, 2000[16]).

Because dilution outside the near-field zone will be provided by both tidal flows and by freshwater inflow to the Bay, it is useful to calculate the "net dilution flow." The net dilution flow is defined as the total flow available for diluting the effluent and accounts for dilution provided both by freshwater flows entering the estuary and by tidal flows. The net dilution flow allows one to estimate the steady-state, long-term impacts of a discharge upon the estuary (outside the near-field zone) and is calculated following the procedures found in Fischer et al. (1979) (see Attachment C).

Using the procedures and values provided in Attachment C, a multi-year average of Net Delta Outflow in the channel near the Equilon refinery discharges is estimated to be just over 25,000 cfs, corresponding to a long-term average net dilution flow of about 35,000 cfs. This is equivalent to a long-term average dilution in the vicinity of the discharges (but outside the near-field zone of initial mixing adjacent to the diffuser) of about 3400:1. This result is consistent with results presented for the Avon and Rodeo diffusers (formerly owned by TOSCO)[17].

Seasonal estimates of the average dilution flow can also be calculated as described in Attachment C. Average "worst-case" conditions correspond to summer or fall (season), when dilution in the vicinity of the Equilon diffuser far-field zone is estimated to be 1000:1. This corresponds to an average net dilution flow in the vicinity of the diffuser of about 10,000 cfs. Average "best-case" conditions are observed to occur in winter, when the average "best-case" net dilution flow in the vicinity of the Equilon discharge is estimated to be 120,000 cfs, corresponding to an average "best-case" dilution of greater than 10,000:1 in the channel near the discharges (again, outside the near-field zone).

Flow Science has conducted very detailed studies of similar discharges into San Francisco Bay and has found that long-term (i.e., steady-state, 120-day average) concentrations of effluent in the Bay are low. One such study was conducted in 1987, for an outfall diffuser operated by Chevron Refining and located at Pt. San Pablo, in San Pablo Bay. This discharge was studied using three methods: a field dye study, which involved the release of dye through the diffuser at an effluent flow rate of 7.5 mgd (11.7

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[16] Interagency Ecological Program (IEP). 2000. Net Delta Outflow as calculated by DWR's DAYFLOW program, with results obtained from http://www.iep.ca.gov/dayflow. Site maintained by Interagency Ecological Program (IEP) Sacramento, CA, and accessed on August 15, 2000.

[17] Declaration and testimony of Susan C. Paulsen, Ph.D., to the State Water Resources Control Board of the State of California in the Matter of the Petitions of Western States Petroleum Association and TOSCO Corporation for Review of Order No. 00-011, as amended by Order No. 00-56 (NPDES No. CA0004961) and Order No. 00-015 (NPDES No. CA0005053).

cfs) over one day; a physical model study, which evaluated effluent concentrations throughout the entire Bay over long time-scales using the Army Corps of Engineers Bay/Delta Hydraulic Model, located at Sausalito; and a numerical modeling study, which evaluated the long-term dilution of a continuous discharge throughout the Bay under both low and high Delta outflow conditions (4,400 cfs and 32,000 cfs, respectively). Results from these studies demonstrated that it takes approximately 120-140 days to establish a steady-state concentration distribution in the Bay-Delta for this discharge. Results also showed that an average effluent discharge of 10 mgd (15.5 cfs) at this location would produce a long-term average (i.e., steady-state) dilution of about 8000:1 in Suisun Bay, about 6000:1 in San Pablo Bay, and a dilution of about 13,000:1 at Oyster Point in the South Bay. While this study was conducted for a discharge located approximately seventeen miles southwest of the Martinez discharge, our experience indicates that results for the Martinez discharge would be similar. These results indicate unambiguously that the Bay has a very large dilution capacity for discharges in the vicinity of San Pablo Bay.

In summary, the Equilon Martinez diffuser is situated in an area of high dilution and tidal flushing. Initial dilution from the diffuser in the near-field averages 30:1 or greater, and average far-field dilution is about 3400:1. Multiple studies that have been conducted on this discharge and on similar discharges all point to the conclusion that there is rapid and significant dilution of discharges from the Equilon Martinez diffuser.

Assimilative capacity and dilution credits for bioaccumulative pollutants

As stated in the tentative order, for pollutants that are both bioaccumulative and on the 303(d) list due to fish tissue concentrations, it is assumed that the receiving water body has no assimilative capacity, and no dilution credit has been allowed in the calculation of final limits[18]. The premise of assigning extremely low discharge limits to the Equilon discharge based upon a lack of "assimilative capacity" makes little sense when detailed information about the Equilon Martinez discharge is reviewed. The amounts of these pollutants that are added by the diffuser are very much lower than the probable error in measuring receiving water concentrations of these pollutants. Indeed, the final limits proposed in the tentative order would result in receiving water concentration increments due to the Equilon discharge that are, in many cases, many orders of magnitude below the lowest currently attainable detection limit, and orders of magnitude lower than the effluent limitations specified. In effect, these effluent limits are equivalent to zero discharge limits.

Because there is substantial dilution of the Martinez Equilon discharge within the estuary (e.g., an average far-field dilution of about 3400:1 as detailed above) and because

[18] See, e.g., finding 42 in the tentative order.

concentrations of most of the pollutants of concern are below detection limits, there would be no way to discern any effect on the concentrations of these constituents in the sediments, in biota, or even in the water column away from the near-field zone. Any decision to reduce outfall effluent concentrations to extremely low levels cannot be justified on scientific mass balance principles. Detailed information on specific contaminants for which assimilative capacity is assumed in the tentative order to be zero is provided below.

Dioxin

Water quality objectives for dioxins and furans are based upon a numeric human health water quality objective (WQO) of 0.014 pg/l for 2,3,7,8-TCDD (based upon consumption of aquatic organisms). Because the waters of Carquinez Strait are 303(d)-listed for dioxin compounds on the basis of concentrations of dioxins and furans in fish tissue, a TMDL limit will ultimately be developed for dioxin. The tentative order specifies an interim limit (which corresponds to the existing permit limit) for dioxin TEQ (as TCDD equivalent) of 0.14 pg/l. The tentative order also specifies a compliance schedule set for November 30, 2011, although the current TMDL listing does not anticipate when the TMDL for dioxin might be completed.

Evaluating compliance with proposed limits is difficult, as past data have shown either dioxin concentrations in effluent that were below detection limits or questionable results due to system contamination. To our knowledge, no data are available for concentrations of dioxins in Bay waters or sediments. However, even the existing effluent limit of 0.14 pg/l, which is below current detection limits, is extremely low. If the Martinez effluent were shown to contain dioxin concentrations of 0.14 pg/l, this would imply a far-field increment of dioxin concentration of 0.000041 pg/l that would result from the Equilon Martinez discharge. Similarly, a discharge of 0.014 pg/l would imply a far-field concentration increment of 0.0000041 pg/l. These concentration increments are four and five orders of magnitude below existing detection limits. Even allowing a 10:1 (or, more appropriately, 30:1) dilution would result in immeasurable, negligible increases in dioxin concentration in the receiving water.

PCBs

Like dioxin, water quality objectives for PCBs are based upon numeric human health criteria. The CTR lists a water quality objective of 0.00017 μg/l, which applies to total PCBs (i.e., the sum of all congener, isomer, homolog, or aroclor analyses)[19]. Carquinez Strait is 303(d)-listed for PCBs on the basis of fish tissue concentrations, and a TMDL is scheduled for completion in 2008. Concentrations of PCBs in Waste 001 have consistently been below detection limits, but all detection limits have been above the WQO. The tentative order found a reasonable potential for PCBs and included an effluent limit for PCBs on the basis that PCBs have been historically present at the facility, detection limits are above the WQO, and PCBs are bioaccumulative, 303(d)-listed pollutants in Carquinez Strait.

The tentative order states that it is believed that the discharger "can immediately comply" with the effluent limitations given in the tentative order. Thus, the limits specified by the permit are final (not interim) limits. The tentative order specifies daily maximum limits and monthly average limits of 0.00034 μg/l and 0.00017 μg/l, respectively, for each of seven aroclor groups (i.e., PCB-1016, PCB-1221, PCB-1232, PCB-1242, PCB-1248, PCB-1254, and PCB-1260). Compliance will initially be based upon a minimum level (ML) of 0.5 μg/l as specified in the SIP[20].

If effluent discharged from the Equilon Martinez diffuser contained the monthly average limit of 0.00017 μg/l (0.17 ng/l, or 170 pg/l) PCBs, the long-term, far-field increment in PCB concentration in the receiving water would be approximately 0.00000005 μg/l (equivalent to 0.00005 ng/l or 0.05 pg/l). By comparison, concentrations of dissolved PCBs in water collected from the Davis Point RMP monitoring location in 1999 ranged from 72 to 99 pg/l sum PCBs[21]. (Note that dissolved and total concentrations of PCBs were measured only at Davis Point and not at Pacheco Creek.) Thus, the concentration increment added by the Equilon Martinez diffuser at the effluent limit in the tentative order would increase receiving water concentrations of dissolved PCBs by approximately 0.07%. Concentrations of total PCBs at Davis Point in 1999 ranged from 148 to 1498 pg/l[22], and the corresponding increment of PCBs added by a discharge of 0.17 ng/l from the Equilon Martinez discharge would be 0.003% to 0.03%. This concentration increment represents an immeasurable and insignificant increase in

[19] Water Quality Standards; Establishment of Numeric Criteria for Priority Toxic Pollutants for the State of California. 40 CFR Part 131, May 18, 2000. At p. 31715-31716.
[20] State Water Resources Control Board, Policy for Implementation of Toxics Standards for Inland Surface Waters, Enclosed Bays, and Estuaries of California. (Phase 1 of the Inland Surface Waters Plan and the Enclosed Bays and Estuaries Plan). 2000.
[21] 1999 Annual Report: San Francisco Estuary Regional Monitoring Program for Trace Substances. San Francisco Estuary Institute, Richmond, CA. At p. 144.
[22] Ibid., at p.147.

receiving water concentrations. Even if a 10:1 (or, more appropriately, 30:1) initial dilution were allowed in calculating the effluent limitation, the Martinez Equilon diffuser would contribute a negligible amount of PCBs to the receiving water. The amount of PCBs that would be added by the diffusers under the monthly average limit contained in the tentative order is very much less than the probable error in the measurement of PCBs in the receiving water. In fact, the extremely low effluent limits listed in the tentative order cannot be justified on the basis of mass balance principles.

Note that concentrations of PCBs in the Sacramento and San Joaquin Rivers occasionally exceed the proposed effluent limits contained in the tentative order. For example, total PCB concentrations as high as 850 pg/l and 762 pg/l were measured in the Sacramento and San Joaquin Rivers, respectively, in April 1994[23]. These two rivers are the primary sources of freshwater to the Delta, and thus are the primary sources of water in Contra Costa Canal, the source of Equilon's intake water. Thus, the source water for Waste 001 may contain elevated concentrations of PCBs.

4,4-DDE and Dieldrin

Carquinez Strait is also 303(d)-listed for both 4,4-DDE and dieldrin, again on the basis of measured concentrations in fish tissues. These two constituents were identified as having a "reasonable potential" based solely upon measured concentrations in the receiving water that were higher than water quality objectives. The tentative order specifies daily maximum concentration limitations (0.00118 μg/l for 4,4-DDE and 0.00028 μg/l for dieldrin) and monthly average concentration limits (0.00059 μg/l for 4,4-DDE and 0.00014 μg/l for dieldrin) based upon numeric human health criteria. Like the effluent limitations for dioxin and PCBs, these are below the detection limits that have been used to date by Equilon. Compliance with these final limits will be based initially on concentrations that are below the minimum levels (MLs) specified in the SIP (2000) (i.e., 0.05 μg/l for 4,4-DDE and 0.01 μg/l for dieldrin). Although Carquinez Strait is 303(d)-listed for these constituents, there is no anticipated date for TMDL completion.

The maximum concentration of 4,4-DDE measured in the receiving water is listed in the tentative order as 0.00069 μg/l (0.69 ng/l, or 690 pg/l), 0.0001 μg/l above the WQO. Measurements of p,p'-DDE concentrations made in 1999 at Davis Point indicated dissolved p,p'-DDE concentrations ranging from 41 to 61 pg/l and total p,p'-DDE concentrations ranging from 88 to 1047 pg/l[24]. Clearly, 4,4-DDE is associated with particles that may be resuspended. Because 4,4-DDE has never been detected in the

[23] 1994 Annual Report: San Francisco Estuary Regional Monitoring Program for Trace Substances. San Francisco Estuary Institute, Richmond, CA. At p. 301.
[24] RMP 1999 at p. 150 and 153.

Equilon Martinez discharge and because this discharge receives significant far-field dilution, there is no evidence that this discharge is in any way responsible for elevated concentrations of 4,4-DDE within the estuary. Further, even a discharge from the Equilon Martinez diffuser at the proposed effluent limitation of 0.00059 μg/l (0.59 ng/l, or 590 pg/l) would result in a concentration increment in the receiving water of only 0.17 pg/l. This concentration increment would correspond to an increase of about 0.28% to 0.4% in dissolved 4,4-DDE concentrations, or an increase of about 0.02% to 0.19% of total 4,4-DDE concentrations in the receiving water. Thus, there is no reason to believe that this low effluent limitation will result in any discernible improvement in 4,4-DDE concentrations in the water column, in sediments, or in biota. Further, this would be true even if an initial dilution of 30:1 were allowed for this constituent. In addition, we note that concentrations of 4,4-DDE in the Sacramento and San Joaquin Rivers at times exceed or approach the proposed effluent limits contained in the tentative order (e.g., concentrations of 920 pg/l and 570 pg/l, respectively, in January 1997[25]). These two rivers are the primary sources of freshwater to the Delta, and thus the primary sources of water in Equilon's intake from the Contra Costa Canal. Thus, the source water for Waste 001 may contain elevated concentrations of 4,4-DDE.

The tentative permit states that the maximum observed concentration of dieldrin in the receiving water is 0.000264 μg/l (0.264 ng/l, or 264 pg/l), 0.000124 μg/l above the WQO. By contrast, concentrations of dieldrin measured in receiving water at Davis Point in 1999 varied from 30 to 85 pg/l (dissolved) and 39 to 110 pg/l (dissolved + particulate)[26]. Thus, all measurements of dieldrin in receiving water in 1999 were below the maximum observed concentration referenced in the tentative order. (Only a single water sample collected from Davis Point has exhibited a dieldrin concentration exceeding 264 pg/l[27] (January 1997, a flood period in the Delta); all other samples collected since 1993 have had total dieldrin concentrations below 150 pg/l.) As with 4,4-DDE, dieldrin has never been detected in the Equilon Martinez discharge and there is no evidence that this discharge is in any way responsible for elevated concentrations of dieldrin within the estuary. Further, even a discharge from the Equilon Martinez diffuser at the proposed effluent limitation of 0.00014 μg/l (0.14 ng/l, or 140 pg/l) would result in a concentration increment in the receiving water of only 0.04 pg/l. This concentration increment would correspond to an increase of about 0.1% in dissolved and total dieldrin concentrations in the receiving water. Thus, there is no reason to believe that this low effluent limitation will result in any measurable improvement in dieldrin concentrations in the water column, in sediments, or in biota. Further, this would be true even if an initial dilution of 30:1 were allowed for this constituent. As with 4,4-DDE, concentrations of dieldrin in the Sacramento and San Joaquin Rivers at times exceed the proposed effluent limits

[25] 1997 Annual Report: San Francisco Estuary Regional Monitoring Program for Trace Substances. San Francisco Estuary Institute, Richmond, CA. At p. A-35.
[26] 1999 RMP at p. 152 and 155.
[27] 1997 RMP at p. A-36.

contained in the tentative order (e.g., concentrations of 380 pg/l and 327 pg/l, respectively, in August 1997[28]). Since water in Equilon's intake originates from these two rivers, the source water for Waste 001 may contain elevated concentrations of dieldrin.

There is no reason to believe that 4,4-DDE or dieldrin were used at the facility or that any site-related activities would result in elevated concentrations of these constituents in effluent discharged from the Equilon Martinez diffuser. Similarly, there is no evidence that the Equilon Martinez discharge is in any way responsible for elevated concentrations of these constituents in receiving waters, sediments, or biota. This conclusion is further supported by a study conducted by Jenkins, Sanders & Associates, which collected and analyzed sediments for the presence of these constituents in sediments near the diffuser and at a background site. This study concluded that "there is no evidence to support the increased accumulation of effluent-related trace elements in the vicinity of the refinery outfall."[29] The inclusion of extremely low effluent limits cannot be justified for either 4,4-DDE or dieldrin on the basis of mass balance considerations.

Mercury

Mercury is listed on the 1998 California 303(d) list for Carquinez Strait on the basis of mercury concentrations in fish tissue. The listing acknowledges that the major source of mercury to this water body is historic and results from gold mining sediments, local mercury mining, and erosion and drainage from abandoned mines. The listing states that point sources are "low to moderate level inputs." As noted in the tentative order, ambient background concentrations of mercury in Central Bay are below both fresh- and salt-water aquatic species water quality objectives (WQOs), but more stringent WQOs, developed to protect human consumption of fish and shellfish, apply.

In the tentative permit, Board staff have chosen to apply an interim mass loading limit of 0.029 kg/month and an interim monthly average effluent limitation of 75 ng/l for mercury. These limits were based upon a statistical analysis of ultraclean mercury data pooled from refinery dischargers in the region[30]. A final mass-based effluent limitation for mercury will be based upon the waste load allocation (WLA) derived from the mercury TMDL. As stated in the tentative order, it is not anticipated that the TMDL will

[28] 1997 RMP, at p. A-36.
[29] Jenkins, Sanders & Associates. Evaluation of concentrations of trace elements and hydrocarbons in sediments adjacent to the outfall of the Shell Oil Martinez Manufacturing Complex. At p. 15.
[30] So, Eddy, California Regional Water Quality Control Board, San Francisco Bay Region. June 13, 2001. Staff report on Statistical analysis of ultraclean mercury data from San Francisco Bay Area refineries.

require "reduction efforts beyond those required by this permit and a separate technical report (13267 letter)."

Background concentrations of mercury have been measured as part of the Regional Monitoring Program (RMP) in the vicinity of the discharge from 1996-1999[31]. For the two stations nearest the Martinez diffuser (i.e., Davis Point and Pacheco Creek), average concentration of dissolved mercury was 0.0021 µg/l (2.1 ng/l). The maximum measured concentration of dissolved mercury at these two stations was 0.0077 µg/l (7.7 ng/l). Even if the limit of mercury (0.029 kg/mo) were discharged continuously via the Martinez diffuser, the increase in the average steady-state mercury concentration at these locations would be at most 0.038 ng/l, or about 0.6%[32].

To put the flux of mercury into perspective, Flow Science compared the diffuser fluxes of mercury to the flux of naturally occurring mercury carried into the Bay with "new" ocean water each day. The concentration of mercury in background ocean water is approximately 5 pmol/kg[33]. This corresponds to a flux of approximately 30 kg/mo of mercury that is carried into the Bay with "new" ocean water. Thus, it is clear that the mass of mercury discharged by the Martinez diffuser is about three orders of magnitude smaller than the mass of mercury brought into the estuary with "new" ocean water every month.

Additionally, it is important to note that a study of effluent-associated contaminants in sediments adjacent to the diffuser[34] found no evidence for the increased accumulation of mercury in sediments in the vicinity of the refinery outfall.

Selenium

Selenium, like mercury, is on the 303(d) list for impairing Carquinez Strait and is considered a bioaccumulative pollutant. In the tentative permit, Board staff have applied an interim effluent concentration (50 µg/l) and mass emission (2.13 lb/day) that are based upon the Settlement Agreement between WSPA and the Board. The tentative order states that these interim limitations will apply until the TMDL for selenium is completed

[31] 1996, 1997, 1998, and 1999 Annual Reports: San Francisco Estuary Regional Monitoring Program for Trace Substances. San Francisco Estuary Institute, Richmond, CA.
[32] This value is calculated assuming that the monthly limit of mercury is discharged continuously into the average flow rate specified in the tentative order (6.7 mgd).
[33] Bruland, K.W. 1983. Trace elements in sea-water. Chapter 45 in: Chemical Oceanography, J.P. Riley and R. Chester, eds. Academic Press: London.
[34] Jenkins, Sanders & Associates. October 13, 1995. Evaluation of concentrations of trace elements and hydrocarbons in sediments adjacent to the outfall of the Shell Oil Martinez Manufacturing Complex.

(anticipated completion date 2010), while the Fact Sheet notes that a five-year compliance schedule of November 30, 2006, will apply for selenium.

Background concentrations of selenium have been measured as part of the Regional Monitoring Program (RMP) in the vicinity of the discharge from 1996-1999[35]. For the two stations nearest the Martinez diffuser (i.e., Davis Point and Pacheco Creek), average concentrations of total selenium were 0.19 µg/l (190 ng/l), and the maximum measured concentration of total selenium was 0.51 µg/l (510 ng/l). Average and maximum dissolved concentrations of selenium at these two locations for the same time period were 0.15 and 0.31 µg/l, respectively. Even if the limit of selenium (2.13 lb/d) were discharged continuously via the Martinez diffuser, the increase in the average steady-state selenium concentration at these locations would be at most 0.01 µg/l, or about 6.7% of the dissolved background concentration and 5.3% of the total background concentration[36]. To help put these numbers in perspective, the concentration of selenium in background ocean water is approximately 1.7 nmol/kg[37]. This corresponds to a flux of approximately 282 lb/d of selenium that is carried into the Bay with "new" ocean water. The limit of 2.13 lb/d in the tentative permit is less than 1% of the natural flux of selenium into the estuary with "new" ocean water on a daily basis. Finally, a study of effluent-associated contaminants in sediments adjacent to the diffuser[38] found no evidence for the increased accumulation of selenium in sediments in the vicinity of the refinery outfall.

Summary

The premise of withholding a dilution credit based upon an "assimilative capacity" or lack thereof makes little sense when detailed information about the Equilon Martinez Waste 001 is reviewed. Several near-field dilution studies have shown that rapid near-field mixing is achieved by the Equilon Martinez diffuser. In fact, it is appropriate to grant a 30:1 dilution (rather than a 10:1 dilution) on the basis of the measured and modeled diffuser performance. Because of the strongly tidal nature of flow in the estuary and past the diffuser location, tidal flushing is significant, and far-field, long-term average dilution is about 3400:1. Thus, there is little opportunity for constituents discharged from the Martinez Equilon diffuser to "build up" within the estuary.

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[35] See annual RMP reports for 1996 through 1999.
[36] This value is calculated assuming that the monthly limit of selenium is discharged continuously into the average flow rate specified in the tentative order (6.7 mgd).
[37] Bruland, K.W. 1983. Trace elements in sea-water. Chapter 45 in: Chemical Oceanography, J.P. Riley and R. Chester, eds. Academic Press: London.
[38] Jenkins, Sanders & Associates. October 13, 1995. Evaluation of concentrations of trace elements and hydrocarbons in sediments adjacent to the outfall of the Shell Oil Martinez Manufacturing Complex.

EPA guidance[39] states that:

> restricting or eliminating mixing zones for bioaccumulative pollutants may be appropriate under conditions such as the following: … Mixing zones might be denied where such denial is used as a device to compensate for uncertainties in the protectiveness of the water quality criteria or uncertainties in the assimilative capacity of the waterbody.

In this case, the effluent limits contained in the final permit are far below current detection limits and significantly lower than chronic continuous criteria (CCC) for bioaccumulative constituents in either freshwater or saltwater. Additionally, there is little uncertainty regarding the assimilative capacity of the receiving water with respect to the Equilon Martinez discharge. Rather, a substantial body of evidence accounts for the complex hydrology of the receiving water and indicates that dilution of this discharge is significant and rapid.

For the bioaccumulative pollutants of dioxin, PCBs, 4,4-DDE, and dieldrin, there is no evidence that discharges from the Martinez Equilon diffuser are in any way responsible for elevated concentrations in receiving waters, sediments, or biota. Similarly, there is no evidence that enforcing the effluent limits given in the tentative permit for these constituents will result in any discernible decrease in concentrations of these constituents in receiving waters, sediments, or biota. Any decision to reduce effluent concentrations of these constituents to the effluent limitations in the tentative permit cannot be justified on scientific mass balance principles. Finally, these arguments also lead to the conclusion that there is no scientific basis for denying a dilution credit for these pollutants.

Sincerely,

Susan C. Paulsen, Ph.D.
Senior Scientist

[39] USEPA, 1991. Technical support document for water quality-based toxics control. EPA/505/2-90-001.

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Critical Review

TOXICITY REFERENCE VALUES FOR METHYLMERCURY EFFECTS ON AVIAN REPRODUCTION: CRITICAL REVIEW AND ANALYSIS

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Abstract: Effects of mercury (Hg) on birds have been studied extensively and with increasing frequency in recent years. The authors conducted a comprehensive review of methylmercury (MeHg) effects on bird reproduction, evaluating laboratory and field studies in which observed effects could be attributed primarily to Hg. The review focuses on exposures via diet and maternal transfer in which observed effects (or lack thereof) were reported relative to Hg concentrations in diet, eggs, or adult blood. Applicable data were identified for 23 species. From this data set, the authors identified ranges of toxicity reference values suitable for risk-assessment applications. Typical ranges of Hg effect thresholds are approximately 0.2 mg/kg to >1.4 mg/kg in diet, 0.05 mg/kg/d to 0.5 mg/kg/d on a dose basis, 0.6 mg/kg to 2.7 mg/kg in eggs, and 2.1 mg/kg to >6.7 mg/kg in parental blood (all concentrations on a wet wt basis). For Hg in avian blood, the review represents the first broad compilation of relevant toxicity data. For dietary exposures, the current data support TRVs that are greater than older, commonly used TRVs. The older diet-based TRVs incorporate conservative assumptions and uncertainty factors that are no longer justified, although they generally were appropriate when originally derived, because of past data limitations. The egg-based TRVs identified from the review are more similar to other previously derived TRVs but have been updated to incorporate new information from recent studies. While important research needs remain, a key recommendation is that species not yet tested for MeHg toxicity should be evaluated using toxicity data from tested species with similar body weights. *Environ Toxicol Chem* 2017;36:294–319. © 2016 SETAC

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INTRODUCTION

Effects of mercury (Hg) on the survival and reproduction of birds have been studied extensively over the last 50 yr [1–3]. Birds can be among the most highly exposed organisms in Hg-contaminated areas as a result of biomagnification of methylmercury (MeHg) through the food web, particularly in aquatic systems. Early research on the effects of Hg on birds was initiated by evidence of bird fatalities related to the use of Hg (often MeHg dicyandiamide) as an agricultural seed dressing [4,5]. With the decline in agricultural Hg uses, ecological risk assessments for Hg now more typically focus on diffuse regional contamination related to atmospheric transport and deposition of Hg and on industrial or mining sites where Hg remains in soil or sediment from historical activities. In its contaminated sediment remediation guidance, the US Environmental Protection Agency (USEPA) [6] estimated that Hg wholly or partially drove decisions at more than 15% of sediment sites remediated under the US Superfund program. Artisanal gold mining is also of concern as an ongoing source of Hg contamination in Africa and South America [7,8].

The predominant practice for predicting risks of adverse effects of Hg on birds involves measuring or estimating Hg exposure in a population of interest and then comparing that exposure to 1 or more toxicity reference values (TRVs). Depending on the application, a TRV may be an exposure level previously shown or estimated to be without deleterious effects, or it may represent a low level of adverse effects. In most cases, TRVs are derived from the peer-reviewed scientific literature, although site-specific avian studies may be conducted to derive TRVs for sites where data indicate that Hg bioaccumulation may be limited by site-specific conditions or where the accuracy of predicted risks has large financial consequences. As an example of the consequences of TRV selection, the Oregon Department of Environmental Quality [9] advises that where Hg concentrations exceed background levels in sediment and specified "acceptable tissue levels" in fish, sediment remedial action should be evaluated. However, sediment remediation, particularly dredging, can itself result in adverse environmental effects as a result of aquatic and riparian habitat disturbance, increased contaminant bioavailability and exposure from sediment resuspension and transport, and carbon emissions from heavy equipment and dredged material transportation. If a TRV is inaccurate, perhaps because it is based on data from an outdated or low-quality study, then significant risks may be overlooked or risks may be significantly overestimated leading to unnecessary environmental costs, which can be substantial.

Extensive data have become available over the past decade to inform the development of Hg TRVs for avian risk assessment. In addition to new studies on aquatic-feeding species [10–14], songbirds have increasingly become a subject of investigation [15]. Another recent development is increasing reliance on blood Hg analyses as a primary tool for monitoring avian Hg exposures [13,14]. Many of the recent studies reflect improvements in study design, analytical methods, effects endpoints, and statistical interpretation compared with older studies that

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historically have been relied on for TRV derivation. In this context, a critical review is warranted to support updated TRVs.

The present article reviews avian ecotoxicology data for Hg, focusing on reproduction as a sensitive endpoint that is directly related to the maintenance of wild bird populations. We comprehensively reviewed the relevant literature and developed criteria for study inclusion in the TRV data set. Because extrapolation of toxicity data to new contexts is inherent in the ecological risk-assessment process, we also reviewed issues relevant to understanding similarities and differences among studies and among species. Based on these findings, we identified ranges of effect thresholds for Hg-related reproductive impairment in birds. These threshold ranges are reviewed in comparison with previously developed TRVs as well as with estimates of naturally occurring, preindustrial background Hg concentrations in avian prey.

LITERATURE REVIEW METHODS

Avian toxicity studies and related literature were identified using Google Scholar and other online searches, reference lists of relevant articles, and direct inquiry to researchers. The literature review methodology was consistent with the principles of systematic review [16], including application of criteria for study inclusion and exclusion; evaluation of the strengths, uncertainties, and potential biases of each study; identification of confidence ratings for each study result; meta-analysis of data where applicable; and transparent documentation of findings. Criteria for inclusion of avian toxicity studies were based on the type of effect measured, specificity in attributing the observed effect to Hg exposure rather than to other stressors, chemical form of Hg, exposure pathways, exposure measures, and data quality. Paired exposure and effects data were compiled for the studies that met the designated criteria.

Study inclusion criteria

Effect endpoints. All studies included in the data compilation measured effects of Hg on reproduction, reflecting a focus on potential population-level effects. Broadly speaking, population success depends on the successful reproduction and survival of individuals, and reproductive effects are more sensitive than mortality in Hg-exposed birds [17,18]. Growth is also sometimes considered for TRV development, but growth effects in Hg-exposed birds are not particularly sensitive [19–21]; and from a population perspective, growth is primarily of interest as a surrogate for reproductive fitness. An alternative option would be to include data for survival, growth, and reproduction in the TRV derivation process [22]; but this approach can add uncertainty if safety factors are applied to results for less sensitive endpoints. For Hg, the available data for avian toxicity are sufficiently robust to support TRVs based specifically on reproductive effects. Although effects on reproductive success can be mediated by various mechanisms (e.g., behavioral or physiological effects), our focus is on the net effect of such processes on reproductive outcomes.

Where available, we considered production of independent offspring (e.g., number surviving through fledging) to be the preferred measure of reproductive success. This endpoint integrates effects on various components of the reproductive process (i.e., fertility, clutch size, hatching success, and fledging success) and is most directly relevant to protection of bird populations. If no measure of the production of independent offspring was reported, we considered various measures of offspring survival, hatching success, fledging success, or nest success. A successful nest is typically defined as a nesting attempt that produces at least 1 fledgling, although in some cases nest success is reported based only on successful hatching of at least 1 egg [23]. Studies that considered multiple avian reproductive endpoints suggested that fecundity expressed as clutch size is relatively insensitive to Hg exposure [4,24,25]; for this reason, studies that evaluated egg production but no other reproductive endpoints were excluded.

Causality. We compiled data from studies where observed effects (if any) could be attributed solely or primarily to Hg exposure, including both controlled experiments and field studies. Although there are unavoidable uncertainties associated with both laboratory and field studies, each provides unique and useful information. Laboratory studies provide controlled conditions to isolate MeHg as the cause of any observed effects. However, laboratories cannot fully replicate natural conditions, and laboratory artifacts can interfere with the interpretation of results. Field studies directly examine effects in the wildlife population of interest, but observed effects may be fully or partially caused by other stressors, such as co-occurring chemicals, low prey availability, poor habitat, depredation, or competition. These factors complicate the attribution of observed adverse effects to Hg and, conversely, can contribute to high variability, which can hinder detection of adverse effects. To assess whether Hg is causing adverse effects in the field, investigators should conduct an equally thorough and transparent analysis of all reasonable candidate causes [26], considering factors such as strength and consistency of association and biological plausibility [27]. Few field studies include any investigation of causality. However, field studies designed to detect effects related to Hg-contaminated sites generally involve observations across a site-related gradient of Hg exposure in which habitat and prey types are intended to be similar in Hg-contaminated and reference locations. Causality is more uncertain in cases where gradients in Hg exposure among birds are not a function of a localized contaminant source but rather a function of factors that influence Hg methylation and/or bioaccumulation (e.g., lake pH, primary productivity, availability of different prey types). For this reason, most of the studies that present a reasonably compelling case for effects caused by Hg were designed to investigate Hg-contaminated sites.

Field studies were excluded from the review if dichlorodiphenyldichloroethylene (DDE) or other chemicals probably caused or contributed substantially to observed effects [28–41], except in 1 case where the authors were able to establish a Hg egg concentration below which adverse effects were not expected despite the observation of DDE-related effects [42]. Certain other studies also were excluded even though Hg was associated with reproductive differences and other chemicals were not identified as likely toxicants. In a study of Bonelli's eagles (*Aquila fasciata*), Ortiz-Santaliestra et al. [43] found greater Hg exposures associated with nests supporting single chicks compared with nests with multiple chicks. This difference was attributed to the confounding effect of coincidentally lower Hg concentrations in the eagles' preferred prey; where the preferred prey species was less abundant, fewer chicks could be supported [43]. We also excluded a study of Hg effects on Acadian flycatchers (*Empidonax virescens*) in central Ohio [44] because the authors did not sufficiently evaluate whether habitat conditions contributed to effects on fledgling production that were marginally correlated with Hg exposure, despite demonstrated adverse effects of urbanization on this species' reproductive success in the same study area [45]. Finally, we excluded studies of black-legged kittiwakes

(*Rissa tridactyla*) in Svalbard, Norway [46,47]. Average prebreeding blood Hg levels were greater in birds that did not breed compared with those that bred; but the differences in average Hg levels between birds with different reproductive outcomes were very small (approximately 0.05 mg/kg wet wt), and there was a high degree of overlap in Hg levels between the 2 exposure groups. Therefore, it appears that Hg is at most a cofactor influencing reproductive outcomes in this kittiwake population. Such a result is consistent with effects related to diet and nutritional factors such as those observed by Ortiz-Santaliestra et al. [43].

Chemical form. In field studies, the form of Hg in avian diets is assumed to vary depending on the type of prey consumed. Mercury in fish is usually 95% to 100% MeHg [48,49], whereas the proportion of total Hg present as MeHg is lower and more variable in invertebrates [1,50,51]. We included controlled experiments in which Hg was administered as MeHg because this form of Hg is environmentally relevant and much more toxic and bioaccumulative than inorganic Hg. Specific MeHg forms included MeHg dicyandiamide, MeHg chloride, and MeHg cysteine. We excluded studies of inorganic Hg toxicity as well as studies using other organomercury forms (e.g., ethylmercury p-toluene sulfonanilide [52]). Total Hg exposures were identified for all field studies, as MeHg often was not measured; however, MeHg exposures are also noted in the data compilation, if measured. Mercury in bird eggs and blood is assumed to be almost exclusively MeHg [53,54].

Exposure pathways. The present review includes studies in which Hg exposures occurred via diet and/or via maternal transfer. Studies using egg injection to expose bird embryos to Hg were excluded because injected MeHg induces adverse effects at lower concentrations than maternally transferred Hg [55,56]. Egg injection is not an environmentally relevant exposure pathway in wild bird populations. Studies that applied Hg externally to eggs also were excluded because the absorbed dose cannot be determined and because it is unknown whether this exposure method would produce dose–response relationships comparable to those observed for Hg exposure via maternal transfer.

Exposure measures. We considered studies in which Hg exposure concentrations were reported for diet, eggs, or parental blood. Food consumption is the major pathway by which birds are exposed to Hg, and dietary Hg is often the primary measure of exposure characterized at Hg-contaminated sites. For laboratory studies, we used measured Hg concentrations if available; otherwise, nominal concentrations were used, and this study limitation is noted. For field studies, uncertainty in characterizing Hg exposure based on dietary Hg lies primarily in prey tissue sampling, which may imperfectly represent true avian dietary preferences. Egg Hg has the advantage of directly representing the exposure of embryos, a particularly sensitive life stage in birds. Parental blood Hg directly represents short-term Hg exposure of parents, with measurable changes occurring within weeks in response to changes in exposure [57]. Parental blood Hg concentrations during breeding provide a nondestructive measure of exposure that may be correlated with egg Hg exposures [14]. Parental blood Hg can also be related to behavioral effects on incubation or provisioning that may affect reproductive outcomes [58,59].

Although trends in avian Hg exposures are sometimes evaluated based on concentrations in feathers, this measure of exposure is generally a poor basis for TRVs. Deposition of Hg in feathers is a protective mechanism that sequesters Hg in nonliving tissue. Birds depurate Hg in their feathers only during feather growth; thus, Hg concentrations in the feathers of migratory birds that molt outside the breeding season reflect exposures in wintering grounds, rather than the more toxicologically important exposure incurred during the breeding season [60]. We also considered nestling blood Hg concentrations to be a poor basis for TRV development. Nestling and parental blood Hg concentrations are not comparable because of rapid nestling growth and MeHg depuration in growing feathers [61]. Too few studies are available to develop TRVs specifically for Hg in nestling blood; and, in any case, nestling blood Hg changes relatively rapidly during development [62], which would be expected to limit comparability among studies.

Data quality. All studies were reviewed for appropriate study design, documentation, and data quality. Although secondary references were reviewed, data were compiled only from primary references. Abstracts were not considered. The present review was consistent with the USEPA's [63] assessment factors for evaluating the quality of scientific information, which include soundness (i.e., the extent to which the study design and methods are appropriate to the researchers' intended application), applicability and utility (i.e., the extent to which the study is appropriate to our intended application), clarity and completeness, appropriate consideration of uncertainty and variability (e.g., through statistical analysis), and evaluation and review by others. Consistent with USEPA guidance for evaluation of ecological toxicity data [64], control performance and documentation of test conditions were reviewed for laboratory studies. Additionally, field studies that lacked a comparable reference site or a wide exposure gradient were excluded because in such cases the study design did not provide a basis to determine whether reproductive outcomes differed from what would be expected in the absence of elevated Hg exposure (i.e., [37,65–73], also osprey [*Pandion haliaetus*] data from Anderson et al. [74] and double-crested cormorant [*Phalacrocorax auritus*] data from Henny et al. [75]).

Study interpretation

Paired exposure and effects data were compiled based on reported Hg concentrations in dietary items, eggs, or blood. We report all Hg concentrations on a wet weight basis. In some cases, it was necessary to estimate wet weight concentrations from dry weight data. If the wet or dry weight basis of Hg concentrations was not reported, we assumed a wet weight basis because that is the most common basis used in the scientific literature for reporting concentrations in biological tissue. All such estimates and assumptions are reported in Tables 1 and 2. Concentrations of MeHg were given stoichiometrically on the basis of Hg content.

Dietary exposures were compiled based on reported Hg concentrations in the diet (as milligrams of Hg per kilogram of food) and on a dose basis (as milligrams of Hg ingested per kilogram of body weight per day). Doses are often calculated in wildlife risk assessments to facilitate integration of exposures experienced through multiple exposure pathways (e.g., food ingestion and sediment ingestion) [76]. Doses were estimated as the product of dietary Hg concentrations and body weight–normalized food ingestion rates. In a few cases, study-specific food ingestion rates were available from Hg toxicity studies [25,77,78], but for most studies it was necessary to estimate a food ingestion rate for the species tested. Species-specific food ingestion rates were identified if available. Otherwise, food ingestion rates were estimated from body weights using regressions developed by Nagy [79] or Kushlan [80]. Adult female body weights were study-specific if available and

Table 1. Methylmercury effects on avian reproduction in controlled experiments

Species	Chemical form	Exposure duration	Diet Hg (mg/kg wet wt)	Hg dietary dose (mg/kg-d)	Egg Hg (mg/kg wet wt)	Parental blood Hg (mg/kg wet wt)	Reproductive endpoint	Effect[a]	Reference	Comments
American kestrel (*Falco sparverius*)	Methylmercury chloride	ca. 60 d	0.16	0.05	1.3	2.5	Expected number of fledglings	EC20	[24]	Blood concentration estimated from diet–blood regression [163]. Exposure to Hg through incubation only. Moderate confidence.
Zebra finch (*Taeniopygia guttata*)	Methylmercury cysteine	2 generations	0.75	0.24	2.7	10	Average no. of offspring	EC20	[85]	Fledging success was more sensitive than clutch size, hatching success, time to renest, and adult survival. Egg Hg from Ou et al. [164]. Companion study reported high intraspecies variability in Hg sensitivity [102]. High confidence.
Ring-necked pheasant (*Phasianus colchicus*)	Methylmercury dicyandiamide	12 wk	0.92	0.06	—	—	Surviving chicks/hen	EC20	[25]	No significant effects on chick mortality. Eggs incubated artificially; does not account for any effects related to incubation behavior. Diet Hg unmeasured. Wet or dry weight basis not reported, but uncertainty is minimal because of low moisture content of grain. Moderate confidence.
Ring-necked pheasant (*P. colchicus*)	Methylmercury dicyandiamide	6–9 d	—	—	0.8/1.35	—	Hatching success	NOAEL/ LOAEL	[4]	Constant dietary dose; egg concentrations increased and hatching decreased over time. Does not account for any posthatching effects. Moderate confidence.
Japanese quail (*Coturnix japonica*)	Methylmercury chloride	2 generations	3.3	0.4	3.9	—	Surviving chicks/egg laid	EC20	[86]	Egg production, fertility, and hatchability were less sensitive than chick mortality. Egg Hg from Eskeland et al. [87]. Egg Hg for experiment 2 estimated from reported concentrations in yolk and albumen. Eggs incubated artificially; does not account for any effects related to incubation behavior. Diet Hg not measured. Wet or dry weight basis not reported for diet or eggs; wet weight assumed. Moderate confidence.
Japanese quail (*C. japonica*)	Methylmercury chloride	16 wk	10	1.2	—	15	Surviving chicks/egg laid	EC80	[96]	Chicks not fed Hg diet; mortality was the result of maternal transfer only. Diet Hg unmeasured. Wet or dry weight basis not reported, but uncertainty is minimal because of low moisture content of grain. Parental blood Hg reported for males only. Moderate confidence.
Black duck (*Anas rubripes*)	Methylmercury dicyandiamide	2 breeding seasons	2.6	0.41	3.86	—	Surviving ducklings/pair	EC80–EC90	[165]	Diet Hg converted to wet weight assuming 10% moisture in feed. Moderate confidence.
Mallard (*Anas platyrhynchos*)	Methylmercury dicyandiamide	2 breeding seasons	2.5	0.4	5.0	5.2	Surviving ducklings/egg	EC20	[77,88–90]	Chick mortality associated with neurological signs of Hg toxicity [104]. No significant effect on fertility or hatching success. Eggs incubated artificially; does not account for any effects related to incubation behavior. Blood Hg estimated from egg–blood regression [166]. Moderate confidence.
Mallard (*A. platyrhynchos*)	Methylmercury chloride	71 d	9.3	1.5	16	17	Surviving ducklings/egg	EC20	[10,92]	Eggs incubated artificially; does not account for any effects related to incubation behavior. Blood Hg estimated from egg–blood regression [166]. High confidence.
Chicken (*Gallus gallus domesticus*)	Methylmercury dicyandiamide	54 d	4.6	0.27	9.5	—	Hatching success	EC70	[78]	Diet Hg (nominal) calculated from Hg in grain and proportion of diet as grain. Wet or dry weight basis not reported for diet, but uncertainty is minimal because of low moisture content of grain. Egg Hg calculated from average Hg mass per egg and egg mass. Moderate confidence.

[a]Doses and EC20s are derived in the present study. Other effects are as reported by authors.
ECx = x% effect concentration; Hg = mercury; NOAEL = no-observed-adverse-effect level; LOAEL = lowest-observed-adverse-effect level.

Table 2. Mercury effects on avian reproduction in field studies[a]

Species	Site and Hg source	Diet Hg (mg/kg wet wt)	Hg dietary dose (mg/kg-d)	Egg Hg (mg/kg wet wt)	Parental blood Hg (mg/kg wet wt)	Reproductive endpoint	Effect	Reference	Comments[b]
American dipper (*Cinclus mexicanus*)	Upper Willamette River watershed, Oregon, USA; mining source	0.04	0.02	0.04	—	Young/territory	NOAEL	[167]	Diet Hg converted from dry weight using study-specific moisture content. In invertebrate prey Hg was 57% MeHg. Small sample size. Unbounded NOAEL below range of effects for all species; limits utility for TRV derivation.
Western/Clark's grebe (*Aechmophorus occidentalis*/*A. clarkii*)	Clear Lake, California, USA; mining source	0.09	0.03	—	—	Young/nest	NOAEL	[74]	Diet Hg from Suchanek et al. [168]. Unbounded NOAEL below range of effects for all species; limits utility for TRV derivation.
Carolina wren (*Thryothorus ludovicianus*)	South River and North Fork Holston River, Virginia, USA; industrial sources	0.21	0.14	0.3	2.13	Nest success (production of ≥1 fledgling)	LOAEL	[110,128]	No significant difference in productivity among successful nests. Diet Hg from Northam et al. [169], converted from dry weight assuming 65% water content in aerial life stages of insects [76]. MeHg was 41% of total Hg in diet (weighted average) [170]. Egg concentration is the grand mean of average clutch Hg [128]. Blood Hg is the mean for 2010 females. Nest success was affected by both increased predation and nest abandonment. Small sample size. Moderate confidence.
Common loon (*Gavia immer*)	120 lakes in Wisconsin, USA, and New Brunswick and Nova Scotia, Canada; enhanced Hg methylation in low-pH lakes	0.21	0.05	2.6	4.3	Maximum productivity of 5-wk-old to 6-wk-old chicks/pair	Threshold	[13]	Quantile regression measured effects relative to maximum productivity; 50% decrease from maximum approximates a threshold for consistent effects. Egg concentration estimated from blood–egg regression [171]. Loons are potentially affected by a combination of Hg exposure and prey availability, both a function of lake pH [118]. Moderate confidence.
Tree swallow (*Tachycineta bicolor*)	6 sites, Maine and Massachusetts, USA; industrial and non–point sources	0.29	0.4	0.6	3	Hatching and fledging success	NOAEL	[12]	No effects on productivity observed across exposure gradient. Blood concentration estimated from blood–egg regression [172]. High confidence.
Tree swallow (*T. bicolor*)	South River, Virginia, USA; industrial source	0.34	0.5	0.63	3.0	Fledglings/nest	LOAEL ≈ EC20	[11,123]	Approximately 20% reduction in number of fledglings in 2 of 3 yr; parental blood Hg estimated as average of 3 yr; effects associated with adverse weather conditions. Attribution of effect to Hg supported by feather analyses of dead versus surviving nestlings [173]. Diet Hg converted from dry wt assuming 65% water content in aerial life stages of insects [76]. Egg concentration estimated from blood–egg regression [172]. Adult survival not affected [17]. High confidence.
Black-crowned night-heron (*Nycticorax nycticorax*)	Carson River, Nevada, USA; mining source	0.45	0.08	1.8	—	Young/nest	NOAEL	[75,174]	Hypothesized effect threshold of 0.8 mg/kg (egg) was not predictive of effects with egg Hg up to 1.8 mg/kg. Offspring production was lower in study area than reference area, but this was not attributed to Hg because of lack of exposure–response relationship for Hg in eggs. Diet Hg is average of stomach contents; effect of digestion on Hg concentration is uncertain. In stomach contents Hg was 98% MeHg. Moderate confidence.
Snowy egret (*Egretta thula*) (drought years only)	Carson River, Nevada, USA; mining source	0.46	0.09	0.8	—	Young/nest	Diet, dose: LOAEL; egg: threshold	[75,174]	Study tested utility of hypothesized effect threshold in eggs (0.8 mg/kg); sample size deemed too small to derive a study-specific effect threshold. Results consistent with hypothesized threshold primarily during drought years. Dietary exposure is based on 1997 stomach contents; in 1997, offspring production was lower in study area than reference area (reference data not reported for other years). Effect of digestion on Hg concentration is uncertain. In stomach contents Hg was 90% MeHg. Moderate confidence.

(*continued*)

Table 2. (*Continued*)

Species	Site and Hg source	Diet Hg (mg/kg wet wt)	Hg dietary dose (mg/kg-d)	Egg Hg (mg/kg wet wt)	Parental blood Hg (mg/kg wet wt)	Reproductive endpoint	Effect	Reference	Comments[b]
Osprey (*Pandion haliaetus*)	Northern Quebec, Canada; enhanced Hg methylation in reservoirs	1.4	0.29	0.22	—	Fledgelings/nest	NOAEL	[175,176]	Dietary concentration of 1.4 mg/kg represents grand mean of estimated exposures; maximum station-specific average prey Hg was 2.4 mg/kg, also with no observed adverse effect. Egg Hg is mean reported for all reservoir stations. In eggs and nestling stomach contents Hg was 90% to 95% MeHg. Prelaying dietary Hg exposure uncertain.[c] Moderate confidence.
Black skimmer (*Rynchops niger*)	Lavaca Bay, Texas, USA; industrial source	—	—	0.46	—	Young/nest	NOAEL	[177]	Offspring production was lower than in reference area, reflecting differential nest success. However, Hg concentrations were the same between nests where no eggs hatched and those where some or all eggs hatched, indicating no effect from Hg. High confidence.
Bald eagle (*Haliaeetus leucocephalus*)	Aleutian archipelago, Alaska, USA; military and non–point sources	—	—	0.5	—	Young/territory	NOAEL	[161]	Eight sites, no effect on productivity across exposure gradient. Egg Hg converted from dry wt assuming 80% moisture content. High confidence.
Bald eagle (*H. leucocephalus*)	Pinchi Lake, British Columbia, Canada; mining source	—	—	—	6.7	Chicks/territory	NOAEL	[61]	Small sample size. Moderate confidence.
American avocet (*Recurvirostra americana*)	San Francisco Bay, California, USA; mining source, enhanced methylation in saline areas	—	—	0.54	1.47	Hatching success and chick mortality	NOAEL	[14,162]	No difference in egg Hg between unhatched eggs and random eggs from successful nests. Sample size 382 eggs. Egg Hg estimated using feather–egg regression for chick down feathers [178]. Parental blood Hg from Ackerman et al. [179]. High confidence.
Merlin (*Falco columbarius*)	Mainland Britain, agricultural source; Orkney and Shetland Islands; source assumed food web–related	—	—	2/0.6	—	Nest success (production of ≥1 fledgling), brood size	NOAEL (islands)/ Threshold (mainland)	[109]	Mainland effect threshold based on breakpoint in dose–response data set. Nest success was 43% lower for nests with egg Hg above identified threshold; brood size also decreased above Hg threshold. Merlins on islands were unaffected. Basis for geographic difference in responses is uncertain; see text. Egg concentrations converted from dry wt using study-specific moisture content. Limited documentation of methods, $n = 55$ clutches. Moderate confidence.
Black-necked stilts (*Himantopus mexicanus*)	San Francisco Bay, California, USA; mining source, enhanced methylation in saline areas	—	—	0.74/1.2	1.5/2.6	Mortality of newly hatched chicks	NOAEL /LOAEL	[14,162]	Egg Hg estimated using feather–egg regression for chick down feathers [178]. Blood concentrations estimated from egg–blood regression [14].[d] Mean egg Hg was 0.74 mg/kg for newly hatched live chicks ($n = 79$) and 1.2 mg/kg for newly hatched dead chicks ($n = 14$). No effect on chick survival after immediate posthatching period. Hatching success also not affected. High confidence.
White-tailed sea eagle (*Haliaeetus albicilla*)	Baltic coast and Lapland, Sweden; regional non–point sources	—	—	1	—	Nest success (production of ≥1 hatchling)	NOAEL	[42]	Any effect of Hg at concentrations >1 mg/kg confounded by DDE. Does not account for any posthatching effects, $n = 57$ clutches. Moderate confidence.
Common tern (*Sterna hirundo*)	Wabigoon–English River system, northwestern Ontario, Canada; industrial source	—	—	1 / 3.65	—	Abundance of fledged young versus unhatched eggs	NOAEL/ severe effect level	[180]	Semiquantitative description; abundant fledged young at NOAEL ($n = 40$ nests), near complete reproductive failure at LOAEL ($n = 37$ nests). Moderate confidence.

(*continued*)

Table 2. (*Continued*)

Species	Site and Hg source	Diet Hg (mg/kg wet wt)	Hg dietary dose (mg/kg-d)	Egg Hg (mg/kg wet wt)	Parental blood Hg (mg/kg wet wt)	Reproductive endpoint	Effect	Reference	Comments[b]
Forster's tern (*Sterna forsteri*)	San Francisco Bay, California, USA; mining source, enhanced methylation in saline areas	—	—	1.4/1.8	3.1/4.2	Hatching success	NOAEL /LOAEL	[14]	Mean egg Hg was 1.4 mg/kg in random eggs from successful nests and 1.8 mg/kg in unhatched eggs (egg Hg adjusted to fresh wet wt basis). Does not account for effects on chick survival (if any). No effects observed on postfledging survival [18]. Blood concentrations estimated from egg–blood regression [14], $n = 298$ eggs. High confidence.
Forster's tern (*S. forsteri*)	Lavaca Bay, Texas, USA; industrial source	—	—	0.4	0.7	Young/nest	NOAEL	[177]	Offspring production was 70% higher than at reference location. High confidence.

[a]Tabulated concentrations represent total Hg exposures. The percentage of Hg as methylmercury (MeHg) is noted in the comments where available.
[b]Doses are calculated in the present study; all other results are as reported by authors. Dose–response information and sample sizes are given in Supplemental Data, Table S7, except as noted herein.
[c]Authors attribute low egg Hg to limited prelaying foraging in reservoirs as a result of partial ice cover. However, similarly low diet-to-egg Hg bioaccumulation in osprey has also been observed elsewhere [40].
[d]Application of sequential regression equations is justified because of the very high r^2 (96%) of the down feather–egg regression.
DDE = dichlorodiphenyldichloroethylene; EC20 = 20% effect concentration; LOAEL = lowest-observed-adverse-effect level; NOAEL: no-observed-adverse-effect level; TRV = toxicity reference value.

otherwise generally identified as averages based on data from the Cornell Lab of Ornithology [81]. The body weights and food ingestion rates used in analyses and their basis are detailed in Supplemental Data, Table S1.

We characterized exposure–response relationships using 2 complementary approaches: dose–response model analysis and bounding or estimation of effect thresholds. We conducted dose–response regression analyses for studies that reported sufficient data representing a range of effect levels. Although we preferred at least 5 dose groups, including a control, we also deemed a pheasant data set with 4 dose groups [25] suitable for regression analysis, based on the range of effect levels and availability of replicate results. Of the available data, only laboratory studies reported the requisite number of exposure groups with paired effects data. Reproductive results were not normalized to control performance, because this adjustment has been shown to produce biased results [82]. This restriction precluded combined regression analysis of results for the same species from multiple studies, in cases where control results differed markedly among studies. It was possible to combine results from multigeneration studies, however, because these studies exhibited similar control performance across generations. Regression analyses were performed with R software using a Poisson model for count variables (i.e., number of offspring) and logistic models for proportion variables (i.e., surviving chicks per egg laid) [83,84]. A 4-parameter logistic model was used to accommodate data sets that indicated an upper asymptote associated with no-effect exposures. For mallards, the 4-parameter model yielded a poor fit, and a simpler 2-parameter model was used. Regression equations (given in Supplemental Data, Tables S2–S6) were used to calculate 20% and 50% effect concentrations (EC20s and EC50s).

We compared dose–response relationships among studies and species by compiling and graphing results for all studies that provided paired exposure and response data for treatment groups (i.e., laboratory dose groups or field study areas). To allow comparisons across species, data were normalized to control or reference performance; this adjustment is appropriate for visualization purposes, as no multispecies regression analysis was performed. The dose–response compilation included studies with fewer than 4 treatments, as well as those studies for which we performed species-specific regression analyses.

Effect thresholds were characterized as EC20s if available. Otherwise, the bounds around presumed toxicity thresholds were identified as no-observed–adverse-effect levels (NOAELs) or lowest-observed–adverse-effect levels (LOAELs). Results that support only a NOAEL or a LOAEL are considered "unbounded." In a few cases, researchers identified specific thresholds below which adverse effects were not observed and above which adverse effects were frequent, and these results were simply identified as "thresholds." The designation of NOAELs, LOAELs, and thresholds generally defers to the original authors' interpretation; the rationale for specific exceptions is discussed in the section *Literature Review Results*. The compilation of effect thresholds includes several field studies that could not be incorporated in the dose–response evaluation because of limited documentation or because results were organized by reproductive outcome (e.g., Hg concentrations in unhatched eggs versus randomly sampled eggs) rather than by treatment (e.g., proportion of individuals affected in different areas).

We assigned each result a confidence level to reflect the fact that the criteria for data quality and demonstration of causality

are applied to a continuum of study characteristics. Characteristics required for a high confidence rating are evaluation of effects from nest establishment through fledging, adequate sample size, potential confounding factors assessed (field studies), Hg exposures measured using modern analytical methods, no other obvious sources of potential inaccuracy or bias noted, and study methods and results well documented. If at least 1 of these criteria was not met but the data were deemed usable for quantitative analysis, the result was assigned a moderate level of confidence. Uncertainties associated with results assigned a moderate level of confidence are further considered as part of the identification and discussion of TRV ranges. Studies interpretable with low confidence were excluded from quantitative analysis based on the data quality criterion but are discussed qualitatively in the Supplemental Data.

LITERATURE REVIEW RESULTS

The studies compiled and evaluated for the present review are described separately for controlled experiments and field studies. For controlled experiments (Table 1), a key focus is the applicability of each study's results to avian exposures in the natural environment. For field studies (Table 2), a key focus is whether any observed adverse effects can be confidently attributed to Hg exposures. Dose–response data for both laboratory and field studies are compiled in Supplemental Data, Table S7.

Controlled experiments

Table 1 summarizes toxicity test results for 7 bird species exposed to MeHg in controlled experiments. Species represented by more than 1 study include ring-necked pheasant (*Phasianus colchicus*), Japanese quail (*Coturnix japonica*), and mallard (*Anas platyrhynchos*). Three or more exposure groups were tested for 5 of the species, including American kestrels (*Falco sparverius*) [24], zebra finches (*Taeniopygia guttata*) [85], ring-necked pheasants [25], Japanese quail [86,87], and mallards [10,77,88–92]. Dose–response relationships are shown on a dietary Hg basis in Figures 1 and 2. Dose–response relationships based on egg and/or blood Hg concentrations, where available, are similar to the diet-based relationships and are provided as Supplemental Data, Figures S1 through S4; underlying data are documented in Supplemental Data, Tables S2 through S6. For the remaining 2 species—black ducks (*Anas rubripes*) and chickens (*Gallus gallus domesticus*)—toxicity thresholds are poorly defined because testing was limited to greater exposures that induced severe effects. The latter studies are informative with respect to dose–response relationships and the relative sensitivity of the test species, although they are not directly usable to estimate toxicity thresholds.

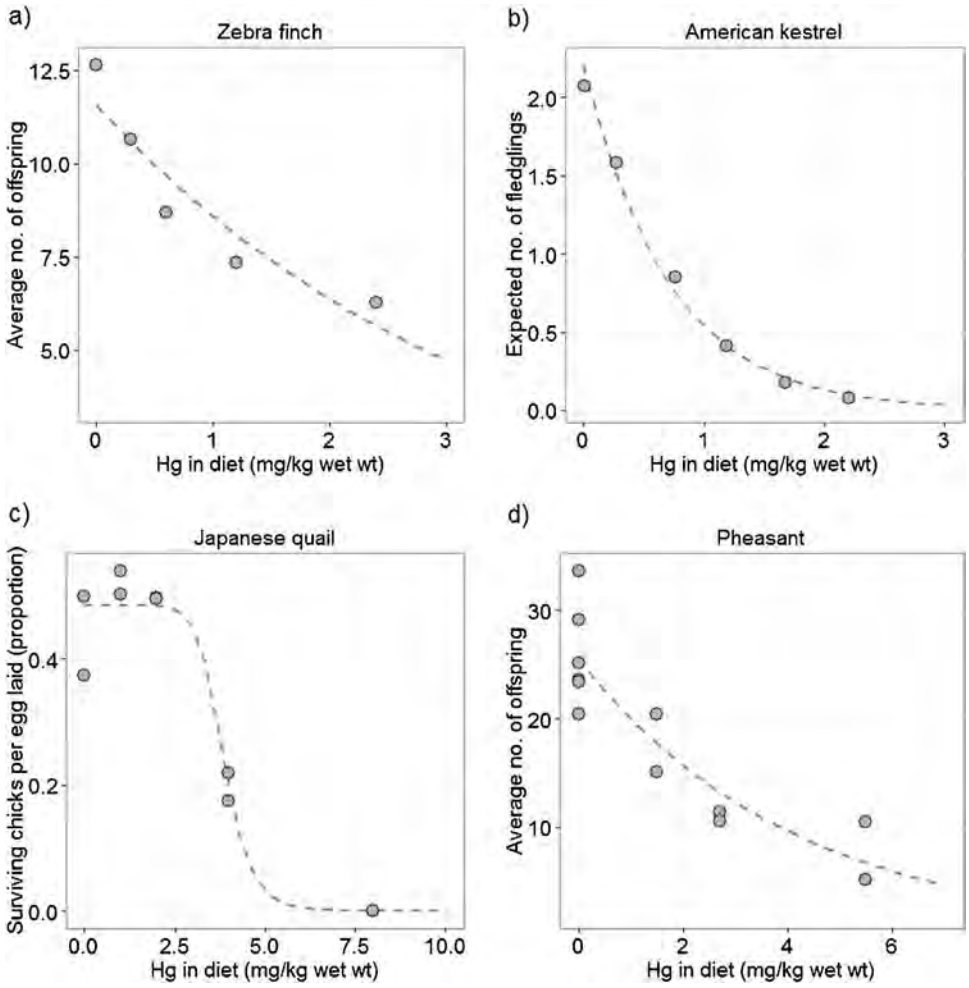

Figure 1. Dose–response relationships for 4 species exposed to methylmercury. Dashed lines represent fitted regressions. (**a**) Zebra finch data [85] represent model averages from generalized linear mixed models, including first- and second-generation pairs. (**b**) For American kestrels, expected number of fledglings accounts for removal of eggs for analysis [24]. (**c**) Japanese quail reproductive success was calculated as % fertility × % hatch × % chick survival (data from Eskeland and Nafstad [86]). (**d**) Pheasant productivity calculated as chicks hatched per hen × % chick survival (data from Fimreite [25]).

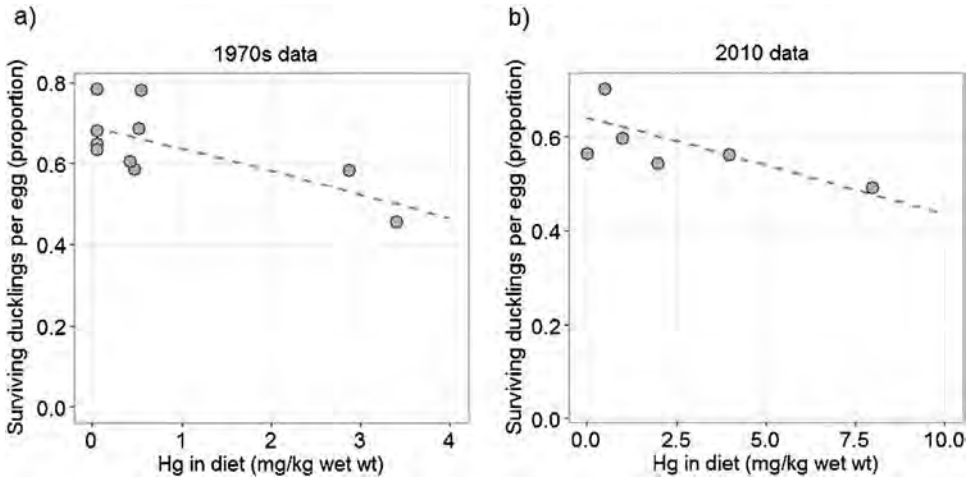

Figure 2. Dose–response relationships for mallards exposed to methylmercury dicyandiamide (1970s) or methylmercury chloride (2010). Dashed lines represent fitted regressions. Response variable calculated as % egg fertility × % hatchability × % duckling survival. Data from Heinz [77,88–90] and Heinz et al. [10,92].

The zebra finch study by Varian-Ramos et al. [85] is viewed with high confidence, as are the results of the mallard study by Heinz et al. [10] once laboratory artifacts related to egg production are factored out (see the section *Mallard studies*). The remaining studies are assigned a moderate confidence rating, in most cases because of study age and historical analytical limitations (or reliance on nominal Hg concentrations). The kestrel study of Albers et al. [24] is assigned a moderate confidence rating because chicks were exposed only via maternal transfer and not via diet. However, even the laboratory studies given a high confidence rating are not without uncertainty. Bioaccessibility of MeHg in laboratory-spiked feed is likely to be greater than that of MeHg that has been biologically incorporated in prey [93]. Also, the ratio of Hg to selenium (Se) in diet is very important because Se protects against Hg toxicity [94], but Hg-to-Se ratios were not reported in spiked feed and may or may not have been realistic (see the section *Extrapolation issues* for further discussion). We also note that the frequently employed practice of artificially incubating eggs eliminates the potential to observe adverse effects on productivity related to parental incubation behavior (nest attentiveness). Adverse effects on hatching success as a result of impaired incubation behavior have been demonstrated for polychlorinated biphenyls [95] and have also been hypothesized as a mechanism by which Hg may cause embryo malposition and subsequent hatching failure in Forster's terns (*Sterna forsteri*) [58]. Lastly, food ingestion rates for laboratory feed may differ from ingestion rates under natural conditions as a result of differing caloric and nutrient contents of dietary items and differing energetic requirements of captive versus free-ranging birds.

Additional discussion is warranted for certain other aspects of the controlled experimental studies, namely, comparison of effects across generations for zebra finches and Japanese quail, comparisons across multiple studies using mallards, and a study using white ibis that is suggestive of possible effects but is not sufficiently conclusive to support TRV derivation. Each of these matters is discussed in the following sections.

Effects on multiple generations. Varian-Ramos et al. [85] observed greater sensitivity in zebra finches that were exposed to Hg throughout their lifetime (i.e., second generation of exposure) compared with finches exposed only as adults (i.e., first generation). The authors posited that combining the results for both generations (Figure 1) is representative of wild populations, which include both immigrants and individuals exposed from conception. Eskeland and Nafstad's [86] study using Japanese quail is noteworthy because it demonstrated selection for Hg tolerance through exposures over 6 generations. The Hg dosage was not consistent across generations, limiting the utility of later generations for TRV development purpose. Doses that were lethal to quail chicks from unexposed parents induced only partial mortality in the chicks descended from quail that had been exposed to moderately toxic Hg doses over several generations. These results illustrate the potential for development of Hg tolerance in bird populations within contaminated areas. For purposes of dose–response analysis, we used data from the first 2 generations. Second-generation chicks consisted of the pooled offspring from the NOAEL and LOAEL dose groups of the first-generation test, which differs from the more typical approach in multiple-generation studies of administering a consistent dosage across generations. However, reproductive responses were generally similar between the first and second generations, and we judged that the uncertainty of including the second-generation results was less than the uncertainty of conducting the regression analysis with 50% fewer data points. An additional Japanese quail study [96] provides results that are generally consistent with those of Eskeland and Nafstad [86], but it could not be included in the regression analysis because the control results were not sufficiently comparable.

Mallard studies. Mallards are the most extensively investigated bird species in experimental studies of MeHg effects on reproduction. Heinz [77,88–90] evaluated effects of a diet containing 0.5 mg/kg Hg as MeHg dicyandiamide on mallard reproduction over 3 generations. A 3 mg/kg exposure was also tested over 2 yr using first-generation birds only [88,89]. The lower dosage has often been identified as a LOAEL [97–100] because production of 1-wk-old ducklings was reduced by 29% ($p < 0.05$) in the second generation only [77]. In the third generation, egg production was 18% lower than the control ($p < 0.05$), but overall duckling production did not differ significantly from control [77]. More recent studies conducted by Heinz et al. [10,92] cast doubt on the identification of 0.5 mg/kg in diet as a reproducible LOAEL for this species.

Heinz et al. [10,92] identified increased productivity (hormesis) in mallards fed a diet containing 0.5 mg/kg Hg in the form of MeHg chloride and observed limited adverse effects even at much greater doses. Hormesis at low Hg exposures was confirmed in a subsequent egg injection study [101].

A limitation common to all the mallard productivity studies cited above is that the authors removed all eggs from the nest for artificial incubation, which stimulated excessive egg production relative to wild populations. Wild ducks typically lay eggs daily until the clutch is complete, whereupon they begin incubating all eggs at the same time. If eggs are removed, the duck will continue to lay; indeed, the total egg production observed by Heinz [77,90] was greatly in excess of the natural production rate [10,92]. Thus, although effects related to egg production rates in the mallard studies could be considered relevant in a livestock production context, with respect to wild birds they are a laboratory artifact.

To further evaluate the implications of artificial incubation on interpretation of the mallard studies, we recalculated the mallard productivity results excluding the egg production endpoint. Specifically, duckling production per egg was identified as the product of egg fertility, hatchability of fertile eggs, and survival of hatchlings. Details are provided in Supplemental Data, Table S6. For exposures up to 1 mg/kg in diet, duckling production per egg was within the range observed for control mallards across studies, even excluding an anomalously low control result from Heinz and Hoffman [91]. At greater exposures, the mallards exposed to MeHg dicyandiamide in the 1970s were more sensitive than those exposed in later studies to MeHg chloride, although without a controlled comparison it is uncertain whether the difference in chemical form was responsible for the difference in toxicological responses. Intraspecies variation is another plausible explanation because the studies used mallards from different sources that may have represented different strains [10,102]. Additionally, analytical methods for quantifying Hg improved considerably after the 1970s [103], such that there is unavoidable uncertainty in Hg concentrations reported from early studies. Animal husbandry practices also may have improved since the 1970s.

We conducted separate analyses of the 2 sets of mallard studies from the 1970s and from 2010. In the 1970s study, the dietary Hg concentration of 2.9 mg/kg caused a statistically significant but small (10%) reduction in duckling survival, an effect accompanied by neurological signs of Hg poisoning and brain lesions [77,89,104]. Greater mortality was associated with exposure to 3.4 mg/kg in diet [88], although Heinz [88] noted uncertainty because of pseudoreplication during that study phase. Based on surviving duckling production per egg, we identified a dietary EC20 of 2.5 mg/kg from that study. In the later MeHg chloride exposures, duckling production per egg was greater than or approximately equal to the control for exposures up to 4 mg/kg in diet, with hormesis observed at a dietary concentration of 0.5 mg/kg [10,92]. We addressed the hormetic results in our regression analysis using methods consistent with those of Folland et al. [105]. Specifically, control results were excluded from the fitted regression but used to define the response level of the EC20 (i.e., 20% lower than the control). This approach yielded an EC20 of 9.3 mg/kg. Results from Heinz and Hoffman [91], an earlier study also using MeHg chloride, could not be included in the regression analysis because of substantially lower control performance. The latter study indicated a severe reduction in reproductive success of mallards exposed to a dietary MeHg concentration of 9.2 mg/kg [91], essentially equal to the EC20 from the later experiment [10,92]. Although the control results from Heinz and Hoffman [91] suggest suboptimal test conditions compared with the other mallard studies, the control-normalized data are included in Supplemental Data, Table S7, for completeness.

Consistent with the marked insensitivity of mallards observed by Heinz et al. [10,92], mallards were among the least sensitive species in a 26-species egg injection study with MeHg [55]. Although egg injection with MeHg produces lower embryotoxicity thresholds than more natural routes of exposure (i.e., diet and maternal transfer) and thus is a weak basis for TRV development, the method may elucidate the relative sensitivity of different species [55]. Also consistent with these findings is a field-based study of duck reproduction at several US National Wildlife Refuges, including a Hg-contaminated area (Lahontan Valley of the Carson River basin, NV, USA) [106]. The authors postulated an egg-based effect threshold for Hg of 0.8 mg/kg wet weight, based on the egg Hg concentration in mallards exposed to 0.5 mg/kg Hg in diet, which the authors identified from Heinz [77] as an unbounded LOAEL. However, Henny et al. [106] observed no difference in hatching success between eggs of multiple duck species containing 3 mg/kg to 9.5 mg/kg dry weight (approximately 0.8–2.4 mg/kg wet wt) compared with eggs with lower Hg concentrations, although the number of samples in the greater concentration range was small [106]. As an additional line of evidence, Heinz and Hoffman [107] evaluated effects of Hg based on concentrations in individual mallard eggs. The lowest egg Hg concentration associated with neurological signs of Hg toxicity in any individual duckling was 2.3 mg/kg, while other ducklings were unharmed despite egg Hg concentrations up to 30 mg/kg. Heinz and Hoffman [107] also evaluated deformities and failure to hatch; but because these conditions also appeared in some control eggs, their cause in individual eggs from Hg-treated mallards could not be definitively determined. In summary, the available data indicate that mallards are relatively insensitive to Hg, with dietary toxicity thresholds of approximately 3 mg/kg to 9 mg/kg.

White ibis study. In addition to the studies summarized in Table 1, a white ibis toxicity study conducted by Frederick and Jayasena [108] would meet the criteria for study inclusion based on study design and documentation; but conclusive interpretation of the study results for TRV development purposes is not possible because of the lack of a clear dose–response relationship and the occurrence of testing artifacts. The study evaluated effects of 3 MeHg chloride treatments on ibis courtship and mating behavior, number of nestlings, and number of fledglings. From the perspective of potential effects on ibis populations, the most relevant of these endpoints is the number of fledglings per female. Although the number of fledglings per female in the low-dose and high-dose groups was nominally lower than the control over 3 breeding yr, the difference was not statistically significant, and the number of offspring fledged per female in the medium-dose group was greater than that of the control. Frederick and Jayasena [108] observed dose-related behavioral effects, most notably male–male pairing. However, male–male pairing also was observed in the control group, even though this behavior has not been reported in wild white ibis at low Hg exposures. Thus, the study reveals an interaction between Hg exposure and captivity, but it is unclear whether the resulting effects on behavior are actually expressed in wild Hg-exposed ibis populations and, if so, whether they occur at a level that would affect overall reproductive success. Frederick and Jayasena [108] also reported that nestling production per female was not

significantly different from that of the control, whereas nestling production per heterosexual male showed a significant difference. The different findings for maternal versus paternal reproductive success are not intuitive but may reflect the occurrence of multiple mating attempts, whereby multiple females eventually mated with the more successful males. In that case, reproductive success would be similar among individual females, but some individual males would register as failing to reproduce. Ultimately it is maternal reproductive success that determines overall productivity and is most critical to population-level effects.

Although Zhang et al. [22] identified the low-dose group in the white ibis study as a reproductive LOAEL, that interpretation is not well supported given that the medium-dose group produced more fledglings per female than the control. On the other hand, we stopped short of identifying the medium-dose or high-dose groups from that study as NOAELs because of the inconsistent results for other reproductive endpoints. Additional investigation is needed to determine the level of Hg exposure that would adversely affect white ibis reproductive success under natural conditions.

Field studies

Table 2 summarizes the results of field studies evaluating Hg effects on reproduction in 16 bird species. Most of the field studies evaluated avian responses to Hg point sources from past industrial, mining, or military operations. Study species included songbirds, raptors, seabirds, shorebirds, wading birds, and other water birds. Species represented by more than 1 field study include tree swallows (*Tachycineta bicolor*), bald eagles (*Haliaeetus leucocephalus*), and Forster's terns. Also, merlin (*Falco columbarius*) results are presented separately for 2 populations that apparently responded very differently to Hg [109], with merlins in mainland Britain exhibiting much greater Hg sensitivity than merlins on the Orkney Islands and Shetland Islands. Merlin brood size on the mainland was not significantly correlated with either DDE or dieldrin metabolite exposures. The authors hypothesized a difference in Hg form, with Hg exposure on the mainland originating primarily from agricultural uses (e.g., MeHg dicyandiamide) and island exposures originating from aquatic food webs. Another possible explanation for the different responses of these merlin populations could have been a difference in Se status (see the section *Extrapolation issues* for further discussion). A third possibility is that the mainland merlins were actually responding not to Hg but rather to differences in available types of prey that happened to contain different Hg levels, as documented recently for Bonelli's eagles [43]. Although we are unable to distinguish these potential causes based on the available data, we provisionally included results for both the mainland and island merlins, recognizing that Hg causality is a significant uncertainty in the mainland data set. In the following sections, we discuss the extensive data available for common loons (*Gavia immer*) and tree swallows, followed by the Carolina wren (*Thryothorus ludovicianus*) study by Jackson et al. [110] (which we interpret differently from the study authors), as well as other field studies that provide supporting information but not stand-alone NOAELs or LOAELs.

Common loon studies. Depew et al. [111] recently reviewed the effects of dietary MeHg on the common loon. The authors proposed an MeHg concentration in prey fish of 0.18 mg/kg as a threshold for significant reproductive impairment in loons, while 0.4 mg/kg was identified as the concentration in fish associated with reproductive failure in wild adult loons. The first of these screening values was derived as the geometric mean of 4 toxicity thresholds [13,112–114]. The inclusion of 1 of these studies [114] relied on extrapolation of egg injection data to a hypothetical dietary concentration and thus did not meet the criteria for inclusion in the present review. Because of the use of quantile regression to address known confounding factors, we consider the analysis by Burgess and Meyer [13] to be the strongest of the available common loon studies, and we have opted to use it to represent common loon sensitivity to MeHg in Table 2. Regardless, both this approach and the Depew et al. [111] synthesis indicate a threshold concentration of approximately 0.2 mg/kg in loon prey.

Although Hg effects on loons have been extensively studied, the exposure–response relationship for this species has not been definitively characterized. Controlled reproductive studies have not been conducted because adult loons fare poorly in captivity. The majority of field studies have focused on loon productivity across regional gradients of Hg exposure, where the observed exposure gradients reflect differential bioaccumulation of atmospherically deposited Hg because of differences in lake pH and other geochemical and landscape factors. However, lake pH and Hg concentrations in fish are also correlated with lake productivity and thus prey availability [115], which in turn influence chick production and survival. Thus, low chick production could be the result of either Hg exposure or low prey availability, and conclusive demonstration of causality is a common challenge to these field studies. Merrill et al. [116] observed loon foraging behavior and the type and size of captured prey across a Hg exposure gradient and concluded that prey availability, rather than Hg exposure, was the factor most likely affecting loon productivity in northern Wisconsin lakes. Indeed, Stafford and Haines [117] and Driscoll et al. [115] identified low lake productivity as a cause of elevated Hg bioaccumulation in fish as a result of low biodilution (i.e., lower growth dilution and/or distribution of the pool of bioavailable MeHg across a smaller total biomass). Kenow et al. [118] identified parental fitness as an additional factor contributing to differences in loon productivity among lakes, with the largest males occupying more desirable (i.e., productive) territories, which also have lower prey Hg levels attributable at least in part to biodilution. Thus, observed correlations do not provide strong evidence of causality and may be specious. The LOAEL identified by Evers et al. [112] for loons in Maine and New Hampshire (0.16 mg/kg in prey) does not account for the characteristic intercorrelation of Hg exposures and prey availability (both a function of lake pH). A recent study of loon reproduction in the Adirondack Mountains (NY, USA) [119] shares the same limitation.

In an evaluation of loon productivity (viable offspring per pair) in Wisconsin and the Canadian Maritimes, Burgess and Meyer [13] addressed confounding factors using quantile regression. This method aims to assess Hg as a limiting factor by quantifying the relationship between maximum productivity and Hg exposure; instances of lower productivity associated with lower Hg exposure are assumed to be caused by other factors. Using quantile regression, Burgess and Meyer [13] calculated an EC50 of 0.21 mg/kg Hg in prey. Although quantile regression is an appropriate tool as applied by Burgess and Meyer [13], even this approach could be confounded if covariance among stressors (e.g., prey productivity and fish Hg concentrations) is sufficiently strong. Also, the term "EC50" as applied to quantile regression results must be interpreted carefully because it represents a 50% decrease compared with the most productive of all loons, not compared with the average

productivity of loons with low Hg exposure. There is a great deal of overlap in productivity distributions between loons exposed to low versus moderate Hg levels in prey, with obvious effects only at exposures exceeding the EC50. This variability is less pronounced when the analysis is carried out using loon blood Hg as the measure of exposure, likely because fish samples are an inexact representation of the species and sizes of prey actually consumed by loons, whereas blood analyses represent loon exposures more directly. Because of the high variability in the exposure–response relationship based on prey Hg concentrations and given Burgess and Meyer's definition of the EC50, Depew et al.'s [111] inclusion of the EC50 from that study for prey-based TRV derivation purposes (rather than the EC20, for example) was appropriate. In Table 2, we identify Burgess and Meyer's [13] EC50 as a "threshold," to avoid confusion with the more typical usage of the term "EC50," namely, an exposure level associated with a 50% reduction in reproductive success compared with average control or reference conditions.

In contrast to the regional studies described, Barr [113] evaluated loon productivity in the vicinity of a point source of Hg (a pulp and paper mill with a chlor-alkali plant) in the Wabigoon–English River system (Ontario), where lake pH was not a confounding factor. However, sudden and frequent dam-related water fluctuations rendered much of the study area essentially unusable for loon nesting regardless of Hg exposure [113], and loons might also have been exposed to other, unmeasured stressors related to pulp and paper mill operations in the vicinity of the Hg source. An association between Hg exposure and reduced productivity remained when water fluctuation–affected nests were removed from the analysis, although the resulting sample size was small ($n = 5$ loon pairs in the LOAEL exposure group). Depew et al. [111] identified a LOAEL of 0.17 mg/kg Hg in prey from that study, based on reported average concentrations in yellow perch (*Perca flavescens*). However, Barr [113] analyzed Hg concentrations in multiple prey species. Although yellow perch are a frequent prey of common loons, they are by no means the only prey [120]. Considering all sampled prey, Barr [113] identified a LOAEL from that study of 0.3 mg/kg to 0.4 mg/kg in prey. Either interpretation is approximately consistent with the toxicity threshold identified from Burgess and Meyer [13].

Depew et al. [111] also evaluated a study of loon productivity in Quebec [121], which demonstrated no correlation between Hg exposure and loon productivity. Because the average prey fish Hg concentration was reported as 0.15 mg/kg [121], Depew et al. [111] considered the lack of effect in that study to be consistent with the TRV derived from the loon studies discussed. By reporting only a single average fish tissue Hg concentration, however, Champoux et al. [121] obscured an important difference between western and eastern Quebec. In part because of differences in lake pH, average Hg concentrations in loon blood (and thus presumably in prey fish) were nearly 5-fold greater in eastern Quebec than in western Quebec [121]. The lack of any discernible effect of Hg on loon productivity in the Quebec study is thus consistent with the observation that there is a high degree of overlap in loon productivity between low and moderate Hg exposures.

In summary, reduced productivity is associated with common loon exposure to Hg at environmentally relevant prey Hg concentrations, but the available field studies do not provide a fully predictive effect threshold. Controlled experimental approaches would benefit the understanding of exposure–response relationships for this species if effective investigative methods could be developed. The recent suggestion of intraperitoneal injections in wild adult female birds as a means of generating varied egg Hg concentrations within a field site [122] may be a useful application in common loons, though further evaluation would be needed to determine whether that practice would replicate important conditions such as the ameliorative effects of Se that are expected to occur with dietary exposures.

Tree swallow studies. For tree swallows, 2 studies examining the effects of similar Hg exposures yielded somewhat different results. Tree swallows exposed to Hg from the South River (VA, USA) exhibited a 20% reduction in productivity that was observable only during 2 of 3 yr, in part because of the role of adverse weather conditions as a costressor [11,123]. In contrast, nearly identical Hg exposures in a 2-yr study of New England tree swallows yielded no adverse effect on hatching or fledging success [12]. While egg Hg concentrations in both of these studies were approximately 0.6 mg/kg, a further study of tree swallow reproduction adjacent to the Carson River (NV, USA) [124] suggests a slightly greater egg-based Hg threshold. Specifically, Custer et al. [124] reported an average Hg concentration of 1 mg/kg in eggs from clutches with 100% hatchability versus an average concentration of 2 mg/kg for clutches with $<100\%$ hatchability. However, the sample size ($n = 5$ nests for each group) was too small to determine whether these results were significantly different [124], and fledging success was not evaluated; therefore, we did not include the study in Table 2.

Carolina wren study. Jackson et al. [110] evaluated Carolina wren reproduction in the floodplains of 2 Hg-contaminated river systems in Virginia (South River and North Fork Holston River) over a period of 4 yr. Wrens were studied upstream and downstream of the historical Hg sources, by monitoring both nest boxes and natural nests. Exposure to Hg was evaluated primarily based on analyses of adult wren blood, although some egg analyses were also conducted. Considering only successful nests (i.e., nests that produced at least 1 fledgling), Jackson et al. [110] identified no significant difference between the study areas and the upstream reference areas in the number of fledglings produced per nest. However, a significant difference was observed in nest success, in part because of parental abandonment of a larger number of nests in the study areas. Jackson et al. [110] used MCESTIMATE software to derive a dose–response relationship based on the 2010 data, estimating nest success as a function of blood Hg concentrations. The resulting dose–response equation was extrapolated to Hg concentrations in eggs, based on a blood–egg regression equation [110]. Several researchers have adopted the EC10 estimates from this dose–response analysis as a means of interpreting both egg and blood Hg concentrations in a variety of bird species [125–127].

Although it is apparent that nest success in 2010 differed between the reference and downstream areas in the Jackson et al. [110] study, there are important limitations in the dose–response relationship developed from the data set. Specifically, the article does not provide sufficient detail to allow the dose–response modeling exercise to be reproduced, and the limited data presented do not agree with the model as presented. The dose–response model predicts that nest success in the references areas should have been between 75% and 80% based on a blood Hg level of 0.2 mg/kg to 0.5 mg/kg wet weight. However, the actual reference area nest success rate is reported as only 60%. Nest success in the study area appears to be predicted more accurately than in reference areas, at least based on

average blood Hg concentrations. Consequently, the slope of the dose–response curve appears to be exaggerated. It is possible that the failure of the model to accurately reflect the underlying data is the result of high sensitivity of the model to individual results when quantifying the likelihood of low-probability outcomes based on limited data. Only a few results fell within a concentration range of 0.5 mg/kg to 1.0 mg/kg [128]; thus, the shape of the exposure–probability curve is not well defined by data in the vicinity of the EC10. Also, in estimating the percent reduction in nest success associated with various Hg exposures, Jackson et al. [110] defined the baseline blood Hg concentration as 0, rather than consistent with reference conditions. Mean blood Hg concentrations in the reference areas were on the order of 0.2 mg/kg to 0.5 mg/kg. The EC10 of 0.7 mg/kg Hg in wren blood was closer to the concentrations in the reference areas than in the study areas, where mean female blood Hg concentrations ranged from 1.96 mg/kg to 3.38 mg/kg.

Nest success by itself is of limited utility as a test endpoint, because it does not account for the fact that many bird species, including Carolina wrens, normally nest more than once per season [23,129]. In fact, nest success and production of fledglings per season often are not correlated [23]. Jackson et al.'s [110] analysis assumes that the success of each nesting attempt is independent of the outcome of the pair's prior nesting attempt(s), but this assumption is not necessarily valid because more experienced breeders may be more likely to lay multiple successful clutches and less experienced breeders may be more likely to establish a first nest in an area susceptible to depredation. Jackson et al. [110] did not report the overall production of fledglings per mated pair, although Jackson and Evers [128] recorded fledgling production by territory during the final year of the same study. Although the latter results suggest production of approximately 1 fledgling fewer per territory (data not shown), the sample size was low ($n = 11$ study area territories); and unlike Jackson et al.'s [110] analysis of nest success, our calculation of fledglings per territory for the present review did not account for observation biases (e.g., the relationship between nest discovery time and probability of observing nest failure).

In addition, Jackson et al. [110] did not evaluate the potential for causative factors other than Hg potentially contributing to the lower nest success rate observed in the study area. Jackson et al. [110] did not consider habitat characteristics, even though nests were monitored in both forested and developed areas. Habitat quality has the potential to affect reproductive success, given that differences in habitat quality may influence susceptibility to disturbance and availability of food. Also, causes of nest failure were recorded only during the last year of the study, and egg predation rates were found to be greater in the study areas than in the reference areas [128]. The dose–response relationship for nest success published by Jackson et al. [110] did not distinguish effects attributable to depredation from those attributable to nest abandonment. The limited available data indicate greater nest abandonment rates and greater egg depredation in the study areas, but the sample sizes for abandoned nests were relatively small (study area $n = 6$ abandoned nests in 4 territories, reference area $n = 2$ abandoned nests in 2 territories). It is not known whether habitat factors or encounters with predators could have contributed to differences in nest abandonment rates. Further, E. Henry (Anchor QEA, Saratoga Springs, New York, personal communication) obtained and reanalyzed the original data and found that nest success rates did not differ between the study and reference areas in 2007 through 2009 and that nest type (natural versus artificial) was a potential confounding factor in 2010.

In summary, although a difference in Carolina wren nest success rates between reference and study areas was sometimes observed, the quantitative dose–response function presented by Jackson et al. [110] does not accurately represent the relationship between Hg exposures and effects at their study sites. Further, the relative contributions of Hg versus other stressors and confounding factors in affecting nest success rates are uncertain, with differential depredation pressure identified as a cofactor. For these reasons, the dose–response function estimated by Jackson et al. [110] is not recommended as a basis for avian Hg TRVs. However, the unbounded LOAEL from that study is provisionally included in the present data compilation (Table 2), recognizing that small sample size and potential costressors are significant limitations.

Other supporting studies. A study of eastern bluebird (*Sialia sialis*) reproduction near the South River (VA, USA) [59] indicated no relationship between maternal blood Hg levels and any measure of reproductive success. A significant correlation was observed between paternal blood Hg and nestling survival. This effect was attributed not to paternal transfer of Hg (indeed, bluebirds are promiscuous) but rather to effects on the ability of males to provide sufficient food for nestlings. Although the results appear consistent with an effect threshold of approximately 1.5 mg/kg in male blood, the authors did not identify any specific effect threshold; and such caution is appropriate because of the small number of male bluebirds with Hg concentrations above this level. Given that the authors did not identify a threshold from their study, we too are cautious about relying on their study as a basis for TRVs.

For marsh wrens (*Cistothorus palustris*) and white-faced ibises (*Plegadis chihi*) breeding at Great Salt Lake (UT, USA), Ackerman et al. [130] found statistically significant differences in Hg concentrations between opportunistically collected eggs from abandoned nests and randomly collected eggs from successful nests (termed "surrogate eggs"). However, the difference in Hg concentration in the 2 groups was small (<0.15 mg/kg), and the eggs consistently contained more Se than Hg on a molar basis, which may ameliorate potential Hg-related effects [56]. Also, the sample size for marsh wrens was small ($n = 6$ for abandoned and failed-to-hatch eggs combined). For both species, an evaluation of nest abandonment rates based on surrogate egg concentrations indicated no significant relationship between egg Hg concentration and nest success. One possible explanation for the apparent discrepancy is that Hg-related nest abandonment occurred primarily during the first week of incubation, before the collection of surrogate eggs, which occurred between incubation day 6 and day 12. However, additional investigation would be required to verify such a specific behavioral effect. Alternatively, factors other than Hg (e.g., differences between sites with respect to habitat, food, shelter, and/or predators) may have influenced nest abandonment behavior in a manner that covaried with egg Hg concentrations. Such differences were taken into account statistically in the surrogate egg evaluation but not in the opportunistic abandoned egg evaluation. For instance, food web differences can be hypothesized as a possible explanation for the observed results [43]. Thus, while the study results are useful for highlighting areas of potential future research, they are not sufficiently conclusive to support identification of NOAELs or LOAELs for TRV derivation purposes. The Great Salt Lake study also reported no evidence of adverse effects of Hg on American avocets (*Recurvirostra americana*), black-necked

stilts (*Himantopus mexicanus*), or Forster's terns, all of which were subject to lower Hg exposures than those identified for the same species in San Francisco Bay [14] (see Table 2).

Three other studies are worth noting despite their exclusion from the present quantitative analysis because of a lack of data from temporally paired reference areas. Great blue herons (*Ardea herodias*) inhabiting Clear Lake (CA, USA) were exposed to 0.56 mg/kg Hg in prey fish and reproduced normally, based on their production of young per successful nest in comparison to regional monitoring data from prior years [70]. Endangered California clapper rails (*Rallus longirostris obsoletus*) exhibited low reproductive success in San Francisco Bay as a result of predation and egg inviability. An assessment of multiple inorganic and organic contaminants identified Hg as the most widespread contaminant potentially contributing to depressed hatching success, with average fresh wet weight egg Hg concentrations in failed-to-hatch eggs ranging from 0.27 mg/kg to 0.79 mg/kg [66]. Herring gulls (*Larus argentatus*) nesting at Clay Lake (Ontario, Canada) exhibited near-complete hatching success, despite egg Hg concentrations up to 15.8 mg/kg. Fledging success was also considered normal compared with past herring gull studies at other sites [71]. Although the interpretation of these studies is too uncertain to use quantitatively for TRV development, the great blue heron results appear consistent with those observed for black-crowned night-herons, whereas the California clapper rail results may be more consistent with those observed for snowy egrets [75]. The reported herring gull exposures are notably high, but these analytical results are particularly uncertain because only first-laid eggs were sampled, analytical methods at the time of the study were less developed than current methods, and the authors did not report whether results were presented on a dry weight or wet weight basis.

Extrapolation issues

In addition to compiling data on Hg toxicity thresholds from avian reproductive studies, we reviewed information relevant to applying those data in ecological risk assessments. In particular, we reviewed available studies related to interspecies differences in sensitivity, considerations related to body weight and dose calculations, bioaccessibility, Hg–Se interactions, and MeHg form.

Interspecies extrapolation is integral to ecological risk assessment because for any given toxicant, species sensitivity has been characterized for only a subset of wildlife species that warrant protection. We discuss 2 factors of particular interest for TRV development: feeding guild and body weight. Feeding guild is important to Hg TRV derivation for birds because there is some evidence that MeHg tolerance may have evolved to a greater extent in piscivores than some other feeding guilds as a result of natural biomagnification of background Hg. Body weight is important because toxicokinetic and toxicodynamic parameters tend to vary as a function of body size.

Mercury tolerance and feeding guild. As reviewed by Robinson et al. [131] and Eagles-Smith et al. [132], birds can detoxify MeHg through demethylation in the liver, with the resulting inorganic Hg being either eliminated or stored as a nontoxic Hg–Se complex. Both MeHg and inorganic Hg can be secreted in bile for elimination in feces. Birds can also depurate MeHg through deposition in feathers, although this mechanism is effective only during periods of feather growth. All of these mechanisms reduce MeHg concentrations in blood and maternal transfer of MeHg to eggs, which in turn may reduce adverse effects on reproduction. Feeding guilds that naturally experience greater MeHg exposure (e.g., piscivores) might thus have evolved more efficient MeHg detoxification [131].

Hepatic demethylation is a dose-dependent process, with increased demethylation efficiency observed above an exposure threshold; both demethylation rates and thresholds vary among species [132]. Hepatic demethylation is thought to be an active process requiring energy input, and the existence of a threshold that triggers this detoxification mechanism is consistent with that requirement [131]. As such, demethylation should be subject to natural selection, with greater demethylation potentially favored in species with higher MeHg exposure, such as predators of large fish. Indeed, ospreys exhibit efficient MeHg demethylation and low diet-to-egg MeHg bioaccumulation [40]. The connection between maternal diet-to-egg transfer and feeding guild has not been confirmed, however, because detoxification processes have been studied primarily in piscivores to date. However, the studies by Robinson et al. [131] and Eagles-Smith et al. [132] suggest that similarity in feeding guild could be an important consideration when extrapolating across species.

Body weight and dose extrapolation. Species body weight affects several parameters relevant to MeHg exposure in birds and other animals, including food ingestion rates and key toxicokinetic processes (absorption, distribution, metabolism, and elimination) [133–136]. Additionally, as an adaptation to flight, small birds (<300–400 g) have proportionally smaller intestines and higher rates of paracellular absorption of nutrients compared with larger birds, which could potentially enhance uptake of water-soluble toxicants [137] such as protein-bound MeHg [138]. Although many aspects of chemical metabolism and toxic responses are not dependent on body weight [134], there is some evidence that longer-lived bird species tend to have greater resistance to oxidative stress [139,140]. Because larger birds tend to have longer life spans and oxidative stress is a mechanism of MeHg toxicity [94], this represents another mechanism by which MeHg exposure–effect relationships could potentially be related to avian body weight.

In North America, ecological risk-assessment practice typically translates the dietary exposures of the toxicity test species to doses, based on species-specific body weights and food ingestion rates. This linear extrapolation approach takes into account differences in food ingestion rates between toxicity test species and species to which TRVs are applied. However, it does not account for differences in elimination rates, which are also related in part to body size, with smaller animals having faster metabolic rates and contaminant elimination rates [133]. In veterinary medicine, it is recognized that linear extrapolation of drug doses among species tends to overdose large animals and underdose small ones [141]; this is analogous to underestimating the effects of a toxicant in large animals and overestimating the effects in small animals. The European Union's environmental standard for Hg in prey tissue was developed directly from dietary concentrations in toxicity studies [100] and does not account for differences in either ingestion rates or elimination rates. Sample et al. [142] found that dose estimation provided no improvement over dietary concentrations in reducing variation in copper toxicity values among species, for either birds or mammals. Although taxonomic similarities in sensitivity are expected, they were evident only when toxicity values were expressed on a dietary concentration basis and not on a dose basis [142]. These findings suggest that dose extrapolation between species of very different body weights (e.g., from loons to songbirds) introduces considerable uncertainty. Also, size-related factors

such as paracellular absorption and oxidative stress resistance suggest that body weight could affect exposure–response relationships when considered on the basis of dietary or tissue MeHg concentrations, in addition to doses.

Bioaccessibility. Several studies have used in vitro methods to assess MeHg bioaccessibility in freshwater fish and seafood potentially consumed by humans. Although results vary widely, bioaccessibility in raw tissue is frequently less than 60% [93,143–145]. He and Wang [93] found that variation in Hg bioaccessibility among species was related to differences in the subcellular distribution of Hg, with Hg bound to heat-stable proteins such as metallothioneins being less bioaccessible than Hg contained in cellular debris. This observation suggests that biologically incorporated MeHg may be less bioaccessible than MeHg in spiked feed prepared for laboratory toxicity tests. Consistent with these findings, Berntssen et al. [146] found that rats fed contaminated fish exhibited greater fecal excretion and less Hg accumulation than rats fed uncontaminated fish spiked with MeHg chloride to the same concentration. Bioaccessibility of MeHg has not been evaluated using methods designed specifically to address avian digestive uptake, but it is reasonable to expect that results of mammalian bioaccessibility investigations are at least qualitatively applicable to birds. Indeed, Kaufman et al. [147] found in vitro estimates of lead bioaccessibility to be very similar between procedures mimicking avian digestive processes and those mimicking mammalian digestive processes. Bioaccessibility differences could contribute to overprediction of risks when extrapolating from laboratory studies to field conditions.

Mercury–selenium interactions. Another complicating factor in interpreting avian Hg exposures is that Hg toxicity depends in part on Se status because Hg and Se can protect against each other's toxicity (i.e., antagonistic interaction) [148,149]. Selenium is a biologically essential element for nervous system function, although it can be toxic to avian reproduction at high concentrations. For a variety of species, the onset of Hg toxicity roughly corresponds to when the molar concentration of Hg exceeds that of Se in tissue or diet [148,150]. The presence of Se can also reduce Hg bioaccumulation [148,149]. Recent evidence suggests that Hg toxicity is the result of Se deficiency because of the sequestration of Se by Hg [94], and thus the presence of an excess of Se guards against Se deficiency caused by this sequestration. As reviewed by Klimstra et al. [56], several studies in birds confirm the generally antagonistic interaction between Se and Hg toxicity. In mallard eggs injected with embryotoxic and teratogenic doses of both Se and Hg, however, the Hg–Se interaction was antagonistic for embryo mortality but approximately additive for deformities [56]. Additional research is needed to further clarify Hg–Se interactions in birds when Se levels approach a toxicity threshold. Despite this uncertainty, Hg–Se ratios are generally interpretable, and their measurement is recommended for future Hg exposure and effect studies.

Methylmercury form. Potential differences in toxicity among different MeHg forms are a source of uncertainty in applying nearly all of the available controlled experimental studies testing MeHg toxicity to birds. Almost no data exist to assess the effects of MeHg form on toxicity. As previously discussed (see *Mallard studies*), Hg toxicity data for mallards suggest that dietary exposure to MeHg dicyandiamide might cause effects at lower doses than MeHg chloride [10,77,92]; without a controlled comparison, however, other explanations can be advanced, such as decreased sensitivity as a result of improvements in animal husbandry since the 1970s. Although MeHg chloride has been considered applicable to present-day food web Hg exposures, Harris et al. [151] determined that Hg in fish exists as MeHg cysteine. And, MeHg chloride is not an ion pair that can be used to introduce "free" MeHg to toxicity test species; rather, the chloride is covalently bound [151]. On the other hand, it appears that MeHg chloride is metabolized to MeHg cysteine in chickens [152]. Varian-Ramos et al. [85] evaluated the toxicity of MeHg cysteine to zebra finches, but zebra finch reproductive responses to other MeHg forms have not been characterized. In an acute fish toxicity test MeHg chloride was more toxic than MeHg cysteine [151], but we identified no chronic comparison of effects of MeHg forms for any species. A controlled comparison of the metabolism and toxicity to wildlife of the cysteine, chloride, and dicyandiamide forms of MeHg would aid interpretation of the available data for TRV derivation purposes.

APPLICATION TO ECOLOGICAL RISK ASSESSMENT

Ecological risk assessments are typically implemented using a tiered approach, beginning with a conservative screening phase to determine whether additional assessment is warranted, followed by a more definitive phase if needed. Corresponding to this tiered approach, TRVs can be developed as screening values or as predictive risk thresholds. The latter are most appropriate for purposes of weighing cost–benefit and risk–benefit trade-offs, as in the case of environmental remediation decisions. In the present review, we describe typical reproductive effect threshold ranges as well as outlying thresholds and severe effect observations. We focus on predictive risk thresholds, although the data compiled herein could also be used to formulate screening values (e.g., using species sensitivity distribution methods or the low end of effect threshold ranges). For specific ecological risk-assessment applications, TRVs should be tailored as closely as possible to the species and the type and degree of effect most relevant to site conditions and management goals.

To help visualize patterns in the available data, we developed 2 sets of graphs based on dose–response data (Figure 3) and effect thresholds (Figure 4) for each exposure metric (i.e., dietary concentration, dietary dose, egg concentration, and blood concentration). Visual inspection of Figure 3 and the range of EC20 values indicates that dose–response relationships tend to show lower interspecies variability when expressed on the basis of tissue Hg concentrations compared with diet-based or dose-based exposures. For Figure 4, we arrayed the toxicity thresholds and bounding estimates from low to high, in a manner analogous to a species sensitivity distribution (recognizing, however, that the effect types and magnitudes are not consistent in this data set). Thresholds and EC20s are shown as circles, while NOAELs and LOAELs are represented by arrows that point toward the presumed toxicity threshold. (That is, the toxicity threshold is presumed to be an unknown Hg concentration or dose that is greater than the NOAEL and/or lower than the LOAEL for each species.) Exposures that caused reproductive impairment of more than 50% compared with controls are indicated with an X; however, such results are omitted for clarity if an EC20 or LOAEL representing less than 50% effect is also available from the same study (as in the case of several controlled experiments). Based on the factors identified as potentially contributing to interspecies differences in Hg sensitivity, we prepared these figures using colors and shading to distinguish species categories based on body weight

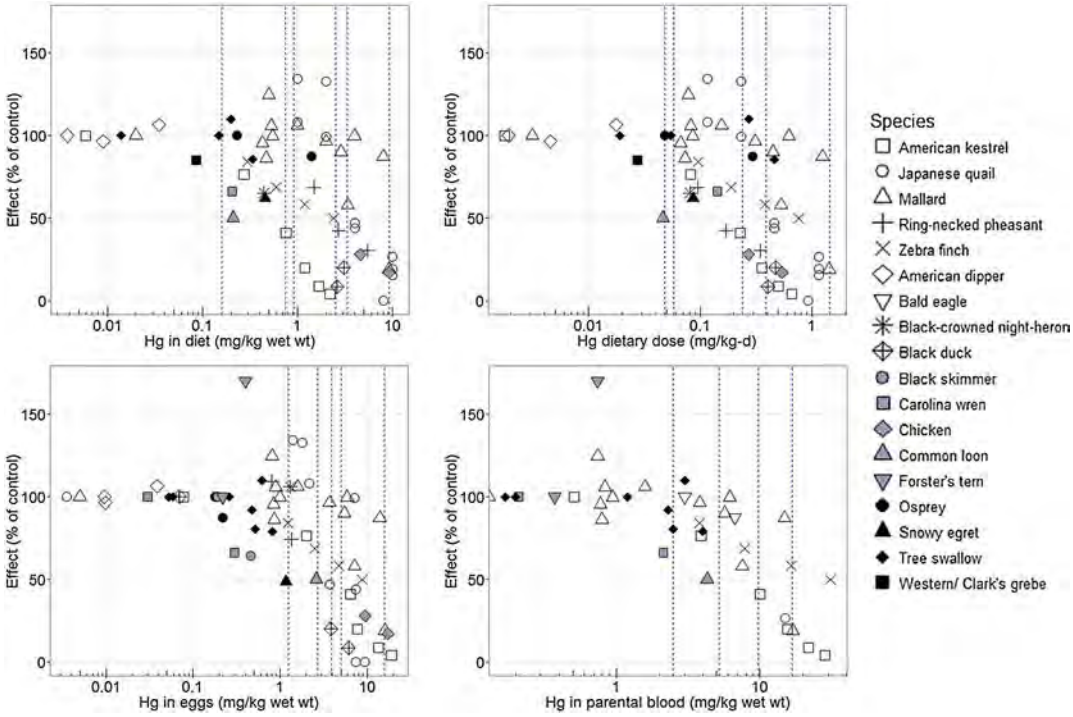

Figure 3. Dose–response data for 18 bird species exposed to methylmercury. Results are measures of reproductive success normalized to control (laboratory) or reference area (field) results for comparability. Vertical lines represent 20% effect concentration values from Table 1.

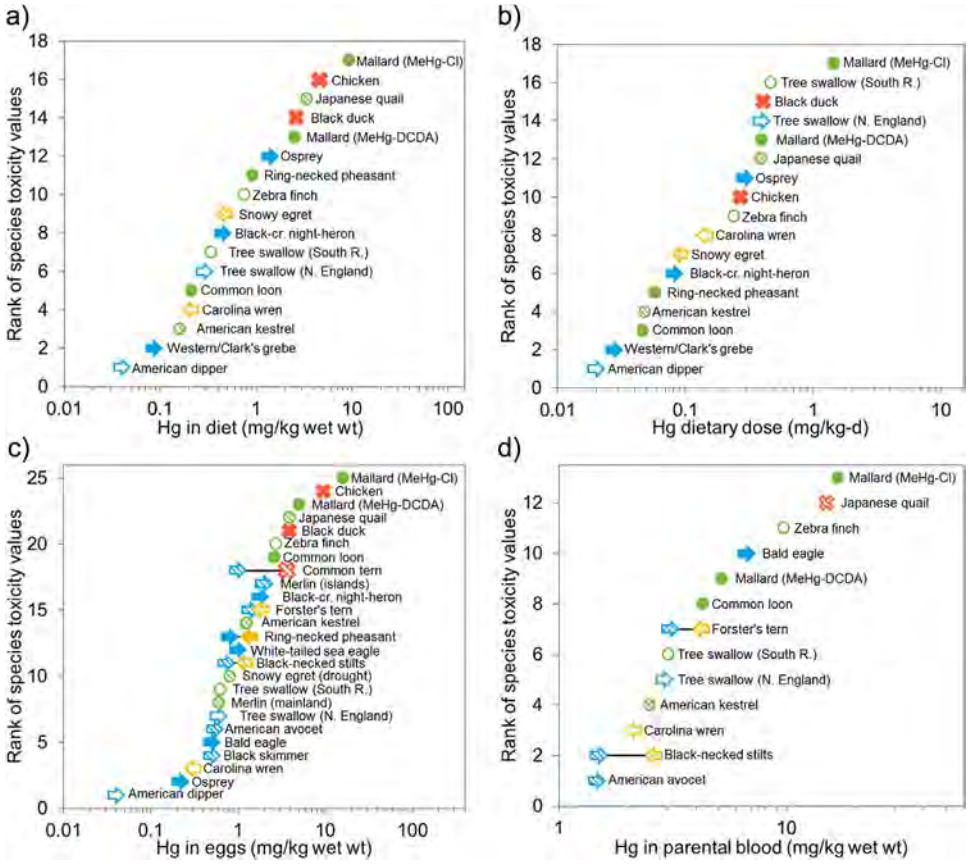

Figure 4. Responses of 23 bird species to methylmercury exposure in laboratory and field studies, based on (**a**) Hg in diet, (**b**) Hg dose, (**c**) Hg in eggs, and (**d**) Hg in parental blood. Blue right-facing arrow indicates no-observed-adverse-effect level; yellow left-facing arrow indicates lowest-observed-adverse-effect level; green circle indicates effect threshold; red X indicates severe effect. Bird size classes are shown as open symbols (small birds, 12–54 g), hatched symbols (medium birds, 120–423 g), and filled symbols (large birds, 794–5500 g).

(Figure 4) and feeding guild (Supplemental Data, Figure S5). Bird size categories were defined as small (12–54 g), medium (120–423 g), and large (794–5500 g), based on natural breaks in the data set as well as the approximate body weight threshold for increased paracellular absorption [137]. Feeding guilds were defined as piscivores, insectivores, omnivores, terrestrial carnivores, and herbivores.

Figure 4 shows that large birds tend to be less sensitive than small or medium-sized birds on the basis of dietary and blood Hg concentrations, with a few exceptions (i.e., common loon and Japanese quail). This difference is somewhat less apparent on an egg Hg basis. Avian body size and taxonomy are not necessarily independent, and thus, it is worth examining whether trends in Hg sensitivity appear more closely related to body size or phylogeny. Although in the present data set the "small" body size category represents only passerine species, the "medium" size category includes 4 different taxonomic orders, and the "large" size category includes 6 orders. It seems unlikely that purely taxonomic differences in sensitivity would coincidentally align with differences in body size, given the large number of orders represented. Conversely, 2 orders are represented by both medium and large species, and these orders present a mixed picture of the relative importance of body size versus taxonomy in affecting MeHg sensitivity. In the Pelecaniformes, the medium-sized species represented in the current data set (snowy egret) exhibits greater sensitivity compared with the large species (black-crowned night-heron). However, in the Galliformes, the medium-sized Japanese quail exhibits sensitivity similar to that observed for larger ring-necked pheasants. It seems likely that both taxonomy and body size may influence sensitivity to MeHg; but overall, the available data support further consideration of body weight in TRV development.

Theoretically, the calculation of dietary doses is supposed to bridge the gap among different size classes of birds by accounting for interspecies differences in food ingestion (and Hg intake) per unit of body weight. Indeed, on a dose basis, the bird size classes are more evenly interspersed with respect to sensitivity. However, if dose calculations accurately reflected differences in Hg intake and elimination, then the sensitivity rankings by dose would resemble those based on tissue Hg because tissue concentrations are a function of Hg intake and elimination rates. In fact, sensitivity rankings based on dose do not resemble those based on egg or blood Hg. For example, tree swallows appear to be moderately sensitive based on their response to Hg on the basis of dietary, egg, and blood Hg concentrations; yet, on a dose basis, they appear highly insensitive. These results suggest that dose-based TRVs for Hg should not be extrapolated among different size classes of birds.

Table 3 summarizes the ranges of effect thresholds and LOAELs by bird size class, as estimated from the available data. Typical ranges and outlying thresholds are identified. Observations of severe effects are also identified and defined for comparison purposes as >50% reproductive impairment relative to controls or reference organisms. The limitations of dose as an exposure metric again are apparent, as dose is the exposure metric for which the observations of severe effects most frequently overlap with the typical range of effect thresholds. Among the effect thresholds identified as extreme values, sensitive outliers include the common loon on a dietary basis and the Carolina wren on an egg basis. The thresholds for both of these species are uncertain because of confounding factors related to prey availability (loons) and predation pressure (wrens). The adverse effect observed in Carolina wrens was related to adult behavior (nest abandonment) rather than embryotoxicity [110]; in fact, on an adult blood basis, the Carolina wren effect threshold does not appear to be an extreme value. Carolina wrens had relatively low egg Hg concentrations relative to blood Hg levels compared with most other species for which both tissue types were evaluated (see Table 2).

At the insensitive end of the spectrum, outlying effect thresholds include the mallard for all exposure metrics, as well as the Japanese quail on a dietary concentration basis and the zebra finch on a blood basis. As previously discussed (see the section *Mallard studies*), multiple lines of evidence indicate that mallards are among the least sensitive species to Hg. Also, the dietary concentrations for both mallards and quail apply to a dry feed mixture, in which both Hg and nutrients may be more concentrated than in a natural diet. Thus, there are substantial uncertainties associated with most of the results identified in Table 3 as extreme values, and these values are not recommended as the basis for predictive risk thresholds to be extrapolated to other species.

Mechanistic studies reviewed by Robinson et al. [131] and Eagles-Smith et al. [132] suggest that feeding guild might affect species sensitivity to Hg. However, sensitivity trends related to feeding guild are not readily apparent on the basis of dietary concentrations, doses, or egg concentrations (Supplemental Data, Figure S5). On the basis of blood concentrations,

Table 3. Summary of estimated reproductive effect thresholds and LOAELs for birds of different size, with severe effect observations shown for comparison

		Hg EC20s, effect thresholds, and LOAELs (mg/kg wet wt)		
Exposure metric	Bird size[a] (*n*)	Typical range	Extreme values	Severe effect observations (mg/kg wet wt)[b]
Diet	Small–medium (6)	0.16–0.75	3.3 (Japanese quail)	0.8–8
	Large (8)	>0.45–>1.4	0.2 (common loon), 2.5–9.3 (mallard)	2.6–9.2
Dose	Small–medium (6)	0.05–0.5	None	0.2–0.9
	Large (8)	0.05–>0.3	0.4–1.2 (mallard)	0.2–0.5
Egg	Small–medium (11)	0.6–2.7	0.3 (Carolina wren), 3.9 (Japanese quail)	1.2–19[c]
	Large (9)	>1–2.6	5.0–16 (mallard)	3.9–17
Blood	Small–medium (7)	2.1–4.2	9.7 (zebra finch)	10–31
	Large (3)	4.3–>6.7	15 (mallard)	17

[a]Bird size ranges are based on average adult female body weight as small = 12–54 g, medium = 120–423 g, and large = 794–5500 g.
[b]Severe effects are defined for comparison purposes as >50% effect compared to control or reference organisms.
[c]Low end of severe effect range is estimated for snowy egret, lower Carson River system, 1997 [75]; data from 2006 in the same system showed no such effect despite higher egg Hg concentrations [174]. Excluding snowy egrets, the severe effect range for egg Hg in small–medium birds is 3.7–19 mg/kg.
EC20 = 20% effect concentration; LOAEL = lowest-observed-adverse-effect level.

piscivores are less sensitive than insectivores; but the number of species in the blood-based analysis is more limited than for other exposure metrics. If similar trends exist on a dietary or egg basis, they may be obscured by differences related to body weight as well as differences in study design and inclusion of unbounded NOAELs and LOAELs in the toxicity data set. Additional research is needed to understand the extent to which feeding guild can be used as a predictor of species sensitivity to Hg.

COMPARISON WITH EXISTING TRVS

Previously published TRVs for protection of birds from the adverse effects of Hg are summarized in Table 4. Most of the previously published TRVs are based on dietary exposures (concentration and/or dose) and derive from seminal TRV development efforts in the 1990s [97,98]. Those original TRVs adopted a conservative interpretation of the mallard studies that were available at the time, and they employed additional uncertainty factors to address data gaps. Two recent publications [3,22] proposed TRVs on the basis of diet and/or tissue based on more current reviews of the avian toxicity literature. Figure 5 compares these previously published TRVs for Hg based on diet, dose, egg, and blood exposures with the reproductive toxicity data set compiled for the present review.

Diet-based and dose-based TRVs

Most of the existing diet-based and dose-based TRVs are lower than the lowest effect thresholds or LOAELs shown in Figure 5, some by more than an order of magnitude. To understand these differences, we review the derivation of the previously published TRVs. Additionally, as a measure of the TRVs' reasonableness, we compare the diet-based TRVs to estimates of preindustrial background Hg concentrations in prey fish. This comparison is appropriate because bird populations have persisted for millennia despite naturally occurring Hg exposures; thus, at least at the population level, Hg exposures at or below levels prevalent over an evolutionary timescale should not be expected to cause adverse effects.

Derivation of existing TRVs. With the exception of the TRVs reported by Zhang et al. [22], all of the diet-based and dose-based TRVs are based on mallard studies by Heinz [77,88–90]. Even though more recent data show that mallards are relatively insensitive to Hg, the mallard-based TRVs derived from Heinz [77,88–90] are lower than necessary for several reasons. First, they are based on identification of the lowest-dose group from the 1970s mallard studies as a LOAEL. This interpretation is not supported by subsequent investigations, and it places undue weight on egg production in studies that used artificial incubation, which induced ducks to lay many more eggs than they would in a natural environment (see the section *Mallard studies*). Second, many of the TRVs incorporate LOAEL to NOAEL and interspecies uncertainty factors to address data gaps, which are no longer applicable given the large amount of avian toxicity data generated since those TRVs were derived. Third, several of the diet-based TRVs entail dose extrapolation from the mallard (a large bird) to much smaller bird species and subsequent back-calculation of diet concentrations for the smaller species. As previously discussed (see the section *Body weight and dose extrapolation*), such dose-based

Table 4. Previously published toxicity reference values (TRVs) for Hg effects on birds

Source (abbreviation)	TRV			Basis per TRV developers[a]
	Hg dose (mg/kg/d)	Hg in diet (mg/kg wet wt)	Hg in avian tissue (mg/kg wet wt)	
Sample et al. [98] (ORNL)	0.0064	0.005	NA	Mallard reproduction LOAEL [77], 10× LOAEL-to-NOAEL uncertainty factor; dose extrapolated to diet of American robin
Zhang et al. [22] (CRAES-SSD)	0.00309	0.00956	NA	SSD, combines multiple end points (biochemical, behavioral, reproductive, mortality); HC5 dose extrapolated to diet of night heron, little egret, and Eurasian spoonbill
Zhang et al. [22] (CRAES-CSA)	0.005	0.01547	0.365 (blood)	White ibis reproduction LOAEL [108], 2× LOAEL-to-NOAEL uncertainty factor; dose extrapolated to 3 species' diet (as above)
USEPA [97,181] (US GLI)	0.013	0.02	NA	Mallard reproduction LOAEL [77], 3× interspecies uncertainty factor, 2× LOAEL-to-NOAEL uncertainty factor; dose extrapolated to diet of belted kingfisher, herring gull, and bald eagle
European Commission [100] (EU)	NA	0.022	NA	Mallard reproduction LOAEL [77], 2× LOAEL-to-NOAEL uncertainty factor, 10× general uncertainty factor
Environment Canada [99] (Canada)	0.031	0.033	NA	Mallard reproduction [77], geometric mean of NOAEL and LOAEL, where NOAEL estimated using 5.6× LOAEL-to-NOAEL uncertainty factor; dose extrapolated to diet of Wilson's storm petrel
Oregon DEQ [9] (Oregon-Ind, Oregon-Pop)	0.013 (Ind), 0.026 (Pop)	0.074 (Ind), 0.15 (Pop)	0.5 (egg, Ind), 2.5 (egg, Pop)	Protection of individual birds based on NOAEL (Ind) and avian populations based on LOAEL (Pop). Doses apparently from USEPA [97]; doses extrapolated to diet of great blue heron. Egg TRV for individuals is bald eagle productivity NOAEL [39]; egg TRV for populations calculated with 5× NOAEL-to-LOAEL uncertainty factor
Ontario Ministry of the Environment [182] (Ontario)	0.064	NA	NA	Mallard reproduction LOAEL as identified by Sample et al. [98]
Shore et al. [3] (Shore-SSD)	NA	NA	0.6 (egg)	Species sensitivity distribution, avian reproduction

[a]The lowest-observed–adverse effect levels and no-observed–adverse effect levels identified by past toxicity reference value (TRV) developers are outdated (mallard), not well supported (ibis), or misidentified (eagle); see text.

ORNL = Oak Ridge National Laboratory; CRAES = Chinese Research Academy of Environmental Sciences; SSD = species sensitivity distribution; CSA = critical study approach; USEPA = US Environmental Protection Agency; GLI = Great Lakes Initiative; DEQ = Department of Environmental Quality; HC5 = hazardous concentration for 5% of species; Ind = individual; Pop = population; LOAEL: lowest-observed-adverse-effect level; NOAEL: no-observed-adverse-effect level; NA = not available.

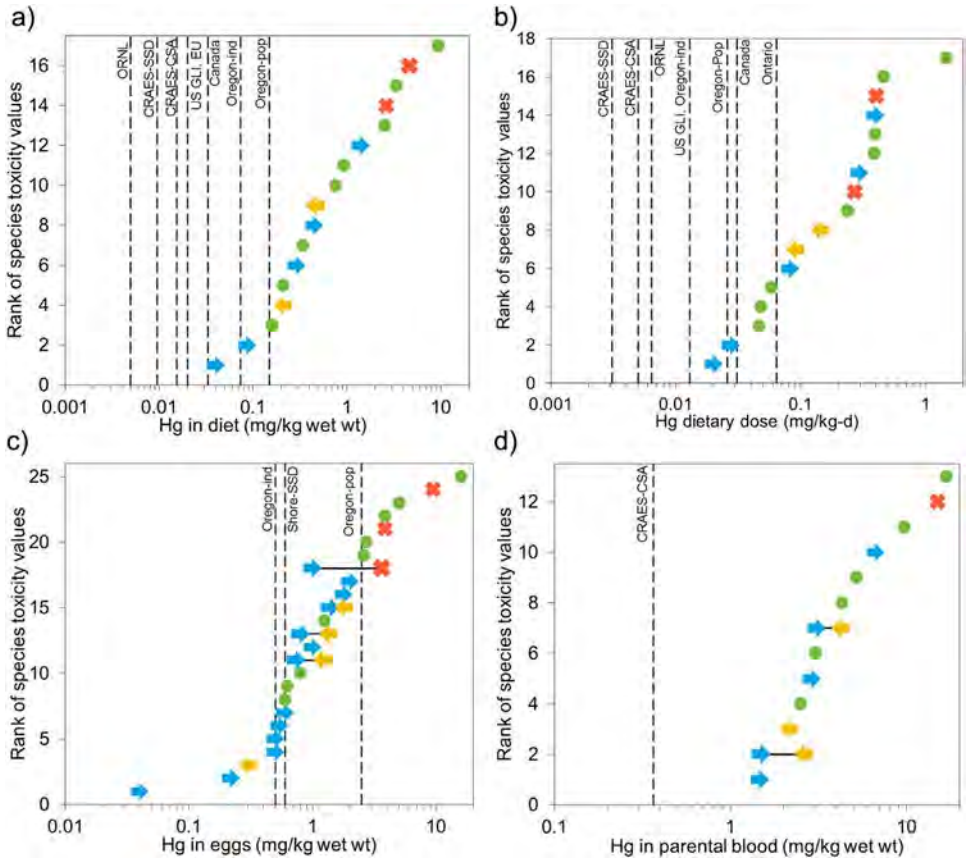

Figure 5. Comparison of previously published toxicity reference values with avian exposure–response data set compiled for the present review, based on (**a**) Hg in diet, (**b**) Hg dose, (**c**) Hg in eggs, and (**d**) Hg in parental blood. Vertical lines indicate toxicity reference values. Blue right-facing arrow indicates no-observed-adverse-effect level; yellow left-facing arrow indicates lowest-observed-adverse-effect level; green circle indicates effect threshold; red X indicates severe effect. TRV sources are shown in Table 4. CRAES = Chinese Research Academy of Environmental Sciences; CSA = critical study approach; EU = European Union; Ind = individual; ORNL = Oak Ridge National Laboratory; Pop = population; SSD = species sensitivity distribution; US GLI = US Great Lakes Initiative.

extrapolations between large and small species tend to distort interspecies sensitivity patterns. Thus, although data limitations meant that the mallard-based TRVs were appropriate at the time they were originally derived, they are now outdated.

Zhang et al. [22] developed avian TRVs for MeHg on behalf of the Chinese Research Academy of Environmental Sciences using 2 approaches: the critical study approach and the species sensitivity distribution approach. The critical study approach is like that used to derive the mallard-based TRVs in that a single toxicity study is identified as being appropriately representative of sensitive species targeted for protection, and the results of that study are adapted using uncertainty factors and interspecies extrapolation methods to develop TRVs. The species sensitivity distribution approach compiles all available and relevant toxicity test results for taxa of interest and then estimates a quantitative species sensitivity distribution function. A target percentile of the distribution function, often the 5th percentile (5% hazard concentration [HC5]), is then selected as the TRV. Both approaches have precedents in existing environmental management arenas. For example, the USEPA uses the critical study approach in the development of toxicity criteria for human health risk assessment and the species sensitivity approach in the derivation of aquatic life criteria for surface water. Although the basic methods are widely accepted, Zhang et al.'s [22] applications of both are problematic.

Using the critical study approach, Zhang et al. [22] identified the white ibis study of Frederick and Jayasena [108] as the most appropriate basis for avian TRVs. As previously discussed (see the section *White ibis study*), that study did not yield a clear dose–response relationship. Although Zhang et al. [22] identified the lowest Hg treatment in that study as a LOAEL, the effect on fledgling production per female was not significant in the lowest treatment group, and it exceeded that of the control in a treatment group receiving greater Hg exposures. Thus, this TRV derivation is inconsistent with the authors' stated methods, which specify that the critical study should demonstrate a clear dose–response relationship for an ecologically relevant endpoint.

For the species sensitivity distribution approach, Zhang et al. [22] compiled NOAELs observed or estimated from controlled experiments for 10 species and used the resultant HC5s to derive dose-based and diet-based TRVs. In principle, the species sensitivity distribution approach provides a useful framework to incorporate a large amount of relevant data. However, the data set compiled by Zhang et al. [22] mixes several different endpoints of varying sensitivity and varying magnitude of effect, ranging from biochemical endpoints to mortality. As a result, the relative sensitivity of the test species to MeHg is not necessarily accurately reflected, and the biological response associated with the HC5 cannot be defined. The inclusion of mortality results is potentially underprotective because reproductive effects tend to be more sensitive than mortality in Hg-exposed birds. Conversely, inclusion of biochemical endpoints adds uncertainty and is potentially overprotective because the magnitude of the response that would correspond to an ecologically relevant effect is unknown.

For this reason, endpoints such as biochemical parameters, immune function, and behavior often are excluded from TRV derivation [153], as they are in the present review. In the case of chicken sensitivity, the magnitude of effect identified by Zhang et al. [22] as a LOAEL (i.e., a 2% decrease in body weight compared with control [154]) is not ecologically relevant. Despite the very small effect reported (i.e., 2%), the chicken LOAEL was divided by a 20-fold uncertainty factor to account for study duration and lack of a NOAEL, causing the chicken to be identified as highly sensitive to MeHg. Such an uncertain datum should have been omitted from the data set. Zhang et al. [22] also included data from a pheasant toxicity test using ethylmercury p-toluene sulfonanilide [52], although the toxicity of this compound relative to MeHg is uncertain. Overall, the most sensitive values in the species sensitivity distribution are questionable for the various reasons presented above, resulting in questionable TRVs.

Comparison with natural background concentrations. Because Hg is naturally occurring (e.g., in volcanic eruptions, natural seeps, geological deposits) and bioaccumulative, there must be a lower limit to the Hg concentrations in prey that could plausibly harm bird populations; that is, TRVs should not be lower than naturally occurring Hg concentrations in the normal prey of the bird species being assessed. However, as reviewed by Fuchsman et al. [155], it is challenging to define naturally occurring Hg concentrations in fish and other avian prey, because Hg released by humans to the environment over centuries has become globally distributed. Fuchsman et al. [155] evaluated 3 lines of evidence relevant to estimating natural background Hg concentrations in prey fish: a modeling exercise by Hope and Louch [156], Hg concentrations in control fish from toxicity experiments [157], and Hg concentrations in fish collected from areas minimally impacted by anthropogenic increases in aerial deposition of Hg and sulfur [158–160]. Sulfur deposition is relevant because it contributes to increases in Hg methylation and subsequent bioaccumulation [115]. These lines of evidence indicated that average naturally occurring Hg concentrations in forage fish are roughly 0.03 mg/kg to 0.1 mg/kg, with greater concentrations (on the order of 0.1–0.3 mg/kg) expected in predatory fish [155]. By this estimate, all of the previously published diet-based avian TRVs for Hg are similar to or lower than naturally occurring Hg concentrations in fish. As such, these TRVs would be expected to overpredict risks to piscivorous birds.

In contrast, the typical diet-based Hg threshold ranges identified in the present review for small to medium-sized birds are slightly greater than estimated naturally occurring Hg concentrations in forage fish, while the typical diet-based threshold ranges for large birds are greater than estimated naturally occurring Hg concentrations in larger fish (Table 3). The data set underlying the typical threshold range for small to medium-sized birds includes few piscivorous species. Thus, it would be more appropriate to compare the diet-based threshold ranges for these bird species to preindustrial background Hg concentrations in invertebrate prey, but no such background estimates are available for comparison. However, most invertebrates and other prey normally contain lower Hg concentrations than are present in fish. In summary, from an evolutionary perspective, the Hg threshold ranges identified in the present review seem more reasonable than previously published diet-based TRVs.

Egg-based TRVs

We identified 3 egg-based TRVs from 2 sources [3,9], all of which fall within the typical threshold range for Hg in eggs. Specifically, Shore et al. [3] identified an HC5 of 0.6 mg/kg. The Oregon Department of Environmental Quality [9] identified egg-based TRVs specifically for protection of ospreys and eagles, with a lower TRV targeting protection of individual birds and a higher TRV targeting protection of populations.

Shore et al. TRV. Shore et al. [3] assembled egg-based NOAELs and LOAELs for Hg effects on reproduction in 19 bird species and applied a species sensitivity distribution approach to the set of LOAELs ($n = 10$). We assembled a substantially different set of egg-based EC20s, NOAELs, and LOAELs for Hg. For example, Shore et al. [3] included a LOAEL of 1 mg/kg in eggs based on older mallard studies, whereas we identified an EC20 from the same studies as 2.5 mg/kg (see the section *Mallard studies*). As another example, Shore et al. [3] included a LOAEL of 1.15 mg/kg for white-tailed sea eagles (*Haliaeetus albicilla*) from Helander et al. [42], but the authors of that study attributed the observed effects to DDE rather than Hg, such that only a NOAEL of 1 mg/kg can be appropriately identified for Hg. Despite differences in the underlying data sets, the Shore et al. [3] TRV is consistent with the exposure–response data compiled in the present review. We identified an effect at an egg concentration lower than 0.6 mg/kg in only 1 of 22 species included in Figure 4, and that LOAEL (for Carolina wrens) is relatively uncertain. The Shore et al. [3] egg TRV is intended to be protective of 95% of species and appears to be consistent with that goal.

Oregon TRVs. Oregon state law requires that TRVs for the protection of bird populations be identified based on LOAEL exposures, whereas TRVs for the protection of individual birds (i.e., for threatened and endangered species) must be identified based on NOAEL exposures. The Oregon Department of Environmental Quality [9] stated that the Hg egg-based TRV for protection of individual birds (0.5 mg/kg) was based on a NOAEL for bald eagle eggs from Wiemeyer et al. [39]. The Oregon Department of Environmental Quality derived the population-level TRV by multiplying the individual-level TRV by a default NOAEL to LOAEL uncertainty factor of 5. In fact, Wiemeyer et al. [39] did not provide a bald eagle NOAEL, although the authors did cite an egg concentration from Wiemeyer et al. [38] for comparison purposes. That comparison value was based on the pheasant toxicity study of Fimreite [25], in which the lowest Hg concentration in pheasant eggs from the LOAEL dose group was 0.5 mg/kg. The identification of this concentration as a NOAEL is thus questionable, and the derivation of a LOAEL from this value using a default uncertainty factor could be underprotective. Nevertheless, the population-based TRV lies within the typical threshold range for Hg in bird eggs. The Oregon Department of Environmental Quality [9] TRV for protection of individual eagles is based on a misinterpretation of historical studies, but it is coincidentally equal to a more recent bald eagle NOAEL [161] and, thus, achieves its target level of protection.

Blood-based TRVs

The present review represents the first broad compilation of avian blood Hg data associated with toxicity studies. As such, only 1 existing blood-based TRV is available for comparison [22], although some researchers have also used the calculated EC10 from Jackson et al. [110] as a basis for comparison (see the section *Carolina wren study*). Zhang et al. [22] identified a blood-based TRV using the critical study approach, based on the white ibis study of Frederick and Jayasena [108]. Analogous to their diet-based TRV, Zhang et al. [22] identified the lowest Hg treatment from that study as a

LOAEL and further modified the corresponding Hg blood concentration with a LOAEL to NOAEL uncertainty factor to identify a TRV (Table 4). As previously discussed (see the section *Diet-based and dose-based TRVs*), this interpretation of the white ibis study is problematic because of the lack of a dose–response relationship or a statistically significant effect on key endpoints. Indeed, the white ibis blood Hg concentration of 0.73 mg/kg would be an outlier compared with the blood Hg results assembled in Figure 4, further supporting our conclusion that this exposure is not a LOAEL. Similarly, the Carolina wren EC10 calculated by Jackson et al. [110] as 0.7 mg/kg is not well supported by the underlying data from that study. The data provisionally support identification of an unbounded LOAEL for Carolina wrens of 2.1 mg/kg Hg in blood, with the recognition that factors other than Hg exposure (e.g., predation pressure, habitat, small sample size) may have affected the results (see the section *Carolina wren study*).

We identified typical ranges of effect thresholds for Hg in avian blood as 2.1 mg/kg to 4.2 mg/kg for small to medium-sized birds and 4.3 mg/kg to >6.7 mg/kg for large birds (Table 3). Studies involving lower Hg exposures found no evidence of adverse effects when parental blood Hg concentrations were 1.5 mg/kg or lower in American avocets and black-necked stilts [14,162]. The bluebird study of McCullagh et al. [59] is also consistent with a lack of adverse effects as a result of adult blood Hg concentrations $\leq$ 1.5 mg/kg, although interpretation of possible effects at greater concentrations in that study was uncertain because of the small number of bluebirds exposed at such levels (see the section *Other supporting studies*). In summary, the data compiled for the present review indicate that Zhang et al.'s [22] blood-based TRV and Jackson et al.'s [110] blood-based EC10 are lower than necessary by factors of approximately 4 and 2, respectively.

CONCLUSIONS

We conducted a comprehensive review of MeHg effects on avian reproduction, using transparent and objective criteria for study inclusion, evaluating uncertainties and biases in each study reviewed and assigning confidence levels to the compiled data. Where multiple studies were available for the same species, we evaluated their consistency and identified possible reasons for inconsistencies where noted. The resulting data set compiles data documenting the occurrence or lack of observed adverse effects attributed to Hg exposure in 23 bird species. We also reviewed information relevant to the extrapolation of these data to other species, including issues related to avian body size and feeding guild as well as Hg bioaccessibility and chemical interactions. Based on the present review, typical ranges of Hg thresholds for adverse effects on avian reproductive success are approximately 0.2 mg/kg to >1.4 mg/kg in diet, 0.05 mg/kg/d to 0.5 mg/kg/d on a dose basis, 0.6 mg/kg to 2.7 mg/kg in eggs, and 2.1 mg/kg to >6.7 mg/kg in parental blood. Within these ranges, the observed thresholds vary for different size classes of birds (Table 3). Severe effects (>50% reduction of reproductive success) are generally limited to exposures greater than the threshold ranges, although this trend is less reliable when exposure is expressed on a dose basis. This analysis is intended to support predictive ecological risk assessments that in turn will support realistic cost–benefit and risk–benefit analyses with respect to environmental decisions such as remediation planning for contaminated sites.

The effect threshold ranges identified in the present review are greater than previously published TRVs on the basis of dietary and blood-based exposures, whereas they are consistent with previously published egg-based TRVs. The discrepancy among diet-based TRVs (including related dose-based TRVs) is primarily the result of past reliance on a conservative interpretation of a mallard toxicity study from the 1970s, which is no longer supportable based on subsequent investigations by the same researchers. Indeed, the continuing widespread reliance on a single, dated mallard study could be viewed as a failure to use available information to advance the science of TRVs and underscores the need for critical review. Certain other TRVs also differ from those proposed in the present review because of specific differences in interpretation of particularly uncertain studies, notably in the identification of a LOAEL for white ibis despite the lack of a dose–response relationship in the subject study. Based on the systematic methodology used and the comparison of TRVs to background Hg concentrations in fish, we contend that the TRVs presented in the present review are more supportable than those previously published by others.

Although MeHg effects on birds have been studied extensively, some important research needs remain. In particular, the interpretation of controlled experimental results would benefit greatly from research to improve the understanding of MeHg bioaccessibility to birds in wild prey versus laboratory-spiked feed. A comparative study of the metabolism and toxicity of MeHg cysteine (the form of MeHg found in fish) versus MeHg chloride and MeHg dicyandiamide is also warranted. Techniques to apply controlled experimental exposures to wild loons are also intriguing because prey availability and Hg exposures are closely intertwined in this key indicator species' habitat, complicating the interpretation of field studies. Further work is needed to improve methods of interspecies extrapolation that limit the distortions introduced by the current practice of applying body weight–normalized doses, which implicitly assumes that body weight–normalized intake governs interspecies differences without regard for differences in elimination rates. Understanding the physiological and genetic bases for differences in sensitivity to MeHg would greatly aid interspecies extrapolation. Research is also needed to clarify interpretation of Hg–Se ratios in birds and their prey, especially when Se concentrations approach a toxicity threshold, although existing data are already sufficient to recommend Se analyses for all Hg exposure and toxicity studies. In the meantime, ecological risk assessors evaluating species not tested for MeHg toxicity should strive to apply toxicity data from species of similar body weight.

Supplemental Data—The Supplemental Data are available on the Wiley Online Library at DOI: 10.1002/etc.3606.

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Data Availability—Data are provided in the online Supplemental Data and in the cited references.

REFERENCES

1. Wiener JG, Krabbenhoft DP, Heinz GH, Scheuhammer AM. 2003. Ecotoxicology of mercury. In Hoffman DJ, Rattner BA, Burton GA Jr, Cairns J Jr, eds, *Handbook of Ecotoxicology*, Lewis, Boca Raton, FL, USA.

2. Chan HM, Scheuhammer AM, Ferran A, Loupelle C, Holloway J, Weech S. 2003. Impacts of mercury on fish-eating wildlife and humans. *Hum Ecol Risk Assess* 9:867–883.
3. Shore RF, Pereira MG, Walker LA, Thompson DR. 2011. Mercury in nonmarine birds and mammals. In Beyer WN, Meador JP, eds, *Environmental Contaminants in Biota: Interpreting Tissue Concentrations*, 2nd ed. CRC, Boca Raton, FL, USA, pp 609–624.
4. Borg K, Wanntorp H, Erne K, Hanko E. 1969. Alkyl mercury poisoning in terrestrial Swedish wildlife. *Viltrevy (Stokh)* 6:301–379.
5. Fimreite N, Karstad L. 1971. Effects of dietary methyl mercury on red-tailed hawks. *J Wildl Manage* 35:293–300.
6. US Environmental Protection Agency. 2005. Contaminated sediment remediation guidance for hazardous waste sites. EPA 540/R-05/012. Washington, DC.
7. Pirrone N, Cinnirella S, Feng X, Finkelman RB, Friedli HR, Leaner J, Mason R, Mukherjee AB, Stracher GB, Streets DG, Telmer K. 2010. Global mercury emissions to the atmosphere from anthropogenic and natural sources. *Atmos Chem Phys* 10:5951–5964.
8. Uryu Y, Malm O, Thornton I, Payne I, Cleary D. 2001. Mercury contamination of fish and its implications for other wildlife of the Tapajós basin, Brazilian Amazon. *Conserv Biol* 15:438–446.
9. Oregon Department of Environmental Quality. 2007. Guidance for assessing bioaccumulative chemicals of concern in sediment. 07-LQ-023A. Portland, OR, USA.
10. Heinz GH, Hoffman DJ, Klimstra JD, Stebbins KR. 2010. Reproduction in mallards exposed to dietary concentrations of methylmercury. *Ecotoxicology* 19:977–982.
11. Hallinger K, Cristol DA. 2011. The role of weather in mediating the effect of mercury exposure on reproductive success in tree swallows. *Ecotoxicology* 20:1368–1377.
12. Longcore JR, Haines TA, Halteman WA. 2007. Mercury in tree swallow food, eggs, bodies, and feathers at Acadia National Park, Maine and an EPA Superfund site, Ayer, Massachusetts. *Environ Monit Assess* 126:129–143.
13. Burgess NM, Meyer MW. 2008. Methylmercury exposure associated with reduced productivity in common loons. *Ecotoxicology* 17:83–91.
14. Ackerman JT, Eagles-Smith CA, Heinz G, De La Cruz SE, Takekawa JY, Miles AK, Adelsbach TL, Herzog MP, Bluso-Demers JD, Demers SA, Herring G, Hoffman DJ, Hartman CA, Willacker JJ, Suchanek TH, Schwarzbach SE, Maurer TC. 2014. Mercury in birds of San Francisco Bay-delta, California—Trophic pathways, bioaccumulation, and ecotoxicological risk to avian reproduction. Open File Report 2014-1251. US Department of the Interior, US Geological Survey, Reston, VA.
15. Jackson AK, Evers DC, Adams EM, Cristol DA, Eagles-Smith C, Edmonds ST, Gray CE, Hoskins B, Lane OP, Sauer A, Tear T. 2015. Songbirds as sentinels of mercury in terrestrial habitats of eastern North America. *Ecotoxicology* 24:453–467.
16. Whaley P, Halsall C, Ågerstrand M, Aiassa E, Benford D, Bilotta G, Coggon D, Collins C, Dempsey C, Duarte-Davidson R, FitzGerald R, Galay-Burgos M, Gee D, Hoffmann S, Lam J, Lasserson T, Levy L, Lipworth S, Ross SM, Martin O, Meads C, Meyer-Baron M, Miller J, Pease C, Rooney A, Sapiets A, Stewart G, Taylor D. 2015. Implementing systematic review techniques in chemical risk assessment: Challenges, opportunities and recommendations. *Environ Int* 92–93:556–564.
17. Hallinger KK, Cornell KL, Brasso RL, Cristol DA. 2011. Mercury exposure and survival in free-living tree swallows (*Tachycineta bicolor*). *Ecotoxicology* 20:39–46.
18. Ackerman JT, Eagles-Smith CA, Takekawa JY, Iverson SA. 2008. Survival of postfledging Forster's terns in relation to mercury exposure in San Francisco Bay. *Ecotoxicology* 17:789–801.
19. Hill EF, Soares JH Jr. 1984. Subchronic mercury exposure in *Coturnix* and a method of hazard evaluation. *Environ Toxicol Chem* 3:489–502.
20. Kenow KP, Gutreuter S, Hines RK, Meyer MW, Fournier F, Karasov WH. 2003. Effects of methyl mercury exposure on the growth of juvenile common loons. *Ecotoxicology* 12:171–182.
21. Fallacara DM, Halbrook RS, French JB. 2011. Toxic effects of dietary methylmercury on immune system development in nestling American kestrels (*Falco sparverius*). *Environ Toxicol Chem* 30:1328–1337.
22. Zhang R, Wu F, Li H, Guo G, Feng C, Giesy JP, Chang H. 2013. Toxicity reference values and tissue residue criteria for protecting avian wildlife exposed to methylmercury in China. *Rev Environ Contam Toxicol* 223:53–80.
23. Etterson MA, Ellis-Felege SN, Evers D, Gauthier G, Grzybowski JA, Mattsson BJ, Nagy LR, Olsen BJ, Pease CM, van der Burg MP, Potvien A. 2011. Modeling fecundity in birds: Conceptual overview, current models, and considerations for future development. *Ecol Model* 222:2178–2190.
24. Albers PH, Koterba MT, Rossmann R, Link WA, French JB, Bennett RS, Bauer WC. 2007. Effects of methylmercury on reproduction in American kestrels. *Environ Toxicol Chem* 26:1856–1866.
25. Fimreite N. 1971. Effects of dietary methylmercury on ring-necked pheasants. Occasional Paper No. 9. Canadian Wildlife Service, Department of Environment, Ottawa, Canada.
26. Norton SB, Rao L, Suter G II, Cormier SM. 2003. Minimizing cognitive errors in site-specific causal assessments. *Hum Ecol Risk Assess* 9:213–229.
27. Hill AB. 1965. The environment and disease: Association or causation? *Proc R Soc Med* 58:295–300.
28. Fleming WJ, Rodgers JA Jr, Stafford CJ. 1984. Contaminants in wood stork eggs and their effects on reproduction, Florida, 1982. *Colonial Waterbirds* 7:88–93.
29. Fyfe RW, Risebrough RW, Walker W II. 1976. Pollutant effects on the reproduction of the prairie falcons and merlins of the Canadian prairies. *Canadian Field-Naturalist* 90:346–355.
30. Gilman AP, Fox GA, Peakall DB, Teeple SM, Carroll TR, Haymes GT. 1977. Reproductive parameters and egg contaminant levels of Great Lakes herring gulls. *J Wildl Manage* 41:458–468.
31. Goutte A, Barbraud C, Meillere A, Carravieri A, Bustamante P, Labadie P, Budzinski H, Delord K, Cherel Y, Weimerskirch H, Chastel O. 2014. Demographic consequences of heavy metals and persistent organic pollutants in a vulnerable long-lived bird, the wandering albatross. *Proc Biol Sci* 281:20133313.
32. Goutte A, Bustamante P, Barbraud C, Weimerskirch H, Delord K, Chastel O. 2014. Demographic responses to mercury exposure in two closely-related Antarctic top predators. *Ecology* 95:1075–1086.
33. Henny CJ, Herron GB. 1989. DDE, selenium, mercury, and white-faced ibis reproduction at Carson Lake, Nevada. *J Wildl Manage* 53:1032–1045.
34. Koeman JH, Hadderingh RH, Buleveld MFIJ. 1972. Persistent pollutants in the white-tailed eagle (*Haliaeetus albicilla*) in the Federal Republic of Germany. *Biol Conserv* 4:373–377.
35. Koivusaari J, Nuuja I, Palokangas R, Finnlund M. 1980. Relationships between productivity, eggshell thickness and pollutant contents of addled eggs in the population of white-tailed eagles *Halieatus albicilla* L. in Finland during 1969–1978. *Environ Pollut A* 23:41–52.
36. Newton I, Bogan JA, Haas MB. 1989. Organochlorines and mercury in the eggs of British peregrines *Falco peregrinus*. *Ibis* 131:355–376.
37. Odsjö T, Sondell J. 1977. Population development and breeding success in the marsh harrier *Cirus aeruginosus* in relation to levels of DDT, PCB, and mercury. *Var Fagelvarld* 236:152–160.
38. Wiemeyer SN, Lamont TG, Bunck CM, Sindelar CR, Gramlich FJ, Fraser JD, Byrd MA. 1984. Organochlorine pesticide, polychlorobiphenyl, and mercury residues in bald eagle eggs—1969–79—and their relationships to shell thinning and reproduction. *Arch Environ Contam Toxicol* 13:529–549.
39. Wiemeyer SN, Bunck CM, Stafford CJ. 1993. Environmental contaminants in bald eagle eggs—1980–84—and further interpretations of relationships to productivity and shell thickness. *Arch Environ Contam Toxicol* 24:213–227.
40. Henny CJ, Kaiser JL, Grove RA. 2009. PCDDs, PCDFs, PCBs, OC pesticides and mercury in fish and osprey eggs from Willamette River, Oregon (1993, 2001 and 2006) with calculated biomagnification factors. *Ecotoxicology* 18:151–173.
41. Tsipoura N, Burger J, Feltes R, Yacabucci J, Mizrahi D, Jeitner C, Gochfeld M. 2008. Metal concentrations in 3 species of passerine birds breeding in the Hackensack Meadowlands of New Jersey. *Environ Res* 107:218–228.
42. Helander B, Olsson M, Reutergårdh L. 1982. Residue levels of organochlorine and mercury compounds in unhatched eggs and the relationships to breeding success in white-tailed sea eagles *Haliaeetus albicilla* in Sweden. *Holarctic Ecology* 5:349–366.
43. Ortiz-Santaliestra ME, Resano-Mayor J, Hernandez-Matias A, Rodriguez-Estival J, Camarero PR, Moleon M, Real J, Mateo R. 2015. Pollutant accumulation patterns in nestlings of an avian top predator: Biochemical and metabolic effects. *Sci Total Environ* 538:692–702.
44. Rowse LM, Rodewald AD, Sullivan SMP. 2014. Pathways and consequences of contaminant flux to Acadian flycatchers (*Empidonax virescens*) in urbanizing landscapes of Ohio, USA. *Sci Total Environ* 485–486:461–467.
45. Bakermans MH, Rodewald AD. 2006. Scale-dependent habitat use of Acadian flycatcher (*Empidonax virescens*) in central Ohio. *Auk* 123:368–382.

46. Tartu S, Goutte A, Bustamante P, Angelier F, Moe B, Clement-Chastel C, Bech C, Gabrielsen GW, Bustnes JO, Chastel O. 2013. To breed or not to breed: Endocrine response to mercury contamination by an Arctic seabird. *Biol Lett* 9:20130317.
47. Goutte A, Barbraud C, Kerzke D, Bustamante P, Angelier F, Tartu S, Clement-Chastel C, Moe B, Bech C, Gabrielsen GW, Bustnes JO, Chastel O. 2015. Survival rate and breeding outputs in a high Arctic seabird exposed to legacy persistent organic pollutants and mercury. *Environ Pollut* 200:1–9.
48. Grieb TM, Driscoll CT, Gloss SP. 1990. Factors affecting mercury accumulation in fish in the upper Michigan peninsula. *Environ Toxicol Chem* 9:919–930.
49. Bloom NS. 1992. On the chemical form of mercury in edible fish and marine invertebrate tissue. *Can J Fish Aquat Sci* 49:1010–1017.
50. Rieder SR, Brunner I, Horvat M, Jacobs A, Frey B. 2011. Accumulation of mercury and methylmercury by mushrooms and earthworms from forest soils. *Environ Pollut* 159:2861–2869.
51. Saxton HJ, Goodman JR, Collins JN, Black FJ. 2013. Maternal transfer of inorganic mercury and methylmercury in aquatic and terrestrial arthropods. *Environ Toxicol Chem* 32:2630–2636.
52. McEwen LC, Tucker RK, Ells JO, Haegele MA. 1973. Mercury-wildlife studies by the Denver Wildlife Research Center. *Proceedings*, Mercury in the Western Environment, Portland, OR, February 25–26, 1971. Oregon State University, Corvallis, OR, USA.
53. Ackerman JT, Herzog MP, Schwarzbach SE. 2013. Methylmercury is the predominant form of mercury in bird eggs: A synthesis. *Environ Sci Technol* 47:2052–2060.
54. Evers DC, Burgess NM, Champoux L, Hoskings B, Major A, Goodale WM, Taylor RJ, Poppenga R, Daigle T. 2005. Patterns and interpretation of mercury exposure in freshwater avian communities in northeastern North America. *Ecotoxicology* 14:193–221.
55. Heinz GH, Hoffman DJ, Klimstra JD, Stebbins KR, Kondrad SL, Erwin CA. 2009. Species differences in the sensitivity of avian embryos to methylmercury. *Arch Environ Contam Toxicol* 56:129–138.
56. Klimstra JD, Yee JL, Heinz GH, Hoffman DJ, Stebbins KR. 2012. Interactions between methylmercury and selenomethionine injected into mallard eggs. *Environ Toxicol Chem* 31:579–584.
57. Ackerman JT, Eagles-Smith CA, Takekawa JY, Bluso JD, Adelsbach TL. 2008. Mercury concentrations in blood and feathers of prebreeding Forster's terns in relation to space use of San Francisco Bay, California, USA, habitats. *Environ Toxicol Chem* 27:897–908.
58. Herring G, Ackerman JT, Eagles-Smith CA. 2010. Embryo malposition as a potential mechanism for mercury-induced hatching failure in bird eggs. *Environ Toxicol Chem* 29:1788–1794.
59. McCullagh EA, Cristol DA, Phillips JB. 2015. Plumage color and reproductive output of eastern bluebirds (*Sialia sialis*) nesting near a mercury-contaminated river. *J Environ Sci Health A* 50:1020–1028.
60. Harris R, Krabbenhoft DP, Mason R, Murray MW, Reash R, Saltman T. 2007. *Ecosystem Responses to Mercury Contamination: Indicators of Change*. CRC, Boca Raton, FL, USA.
61. Weech SA, Scheuhammer AM, Elliott JE. 2006. Mercury exposure and reproduction in fish-eating birds breeding in the Pinchi Lake region, British Columbia, Canada. *Environ Toxicol Chem* 25:1433–1440.
62. Ackerman JT, Eagles-Smith CA, Herzog MP. 2011. Bird mercury concentrations change rapidly as chicks age—Toxicological risk is highest at hatching and fledging. *Environ Sci Technol* 45:5418–5425.
63. US Environmental Protection Agency. 2003. A summary of general assessment factors for evaluating the quality of scientific and technical information. EPA 100/B-03/001. Science Policy Council, Washington, DC.
64. US Environmental Protection Agency. 2011. Evaluation guidelines for ecological toxicity data in the open literature. [cited 2016 April 12]. Available from: http://www.epa.gov/pesticide-science-and-assessing-pesticide-risks/evaluation-guidelines-ecological-toxicity-data-open
65. Hargreaves AL, Whiteside DP, Gilchrist G. 2010. Concentrations of 17 elements, including mercury, and their relationship to fitness measures in Arctic shorebirds and their eggs. *Sci Total Environ* 40B:3135–3161.
66. Schwarzbach SE, Albertson JD, Thomas CM. 2006. Effects on predation, flooding, and contamination on reproductive success of California clapper rails (*Rallus longirostris obsoletus*) in San Francisco Bay. *Auk* 123:45–60.
67. Custer TW, Custer CM, Johnson KM, Hoffman DJ. 2008. Mercury and other element exposure to tree swallows (*Tachycineta bicolor*) nesting on Lostwood National Wildlife Refuge, North Dakota. *Environ Pollut* 155:217–226.
68. Custer TW, Custer CM, Thogmartin WE, Dummer PM, Rossman R, Kenow KP, Meyer MW. 2012. Mercury and other element exposure in tree swallows nesting at low pH and neutral pH lakes in northern Wisconsin USA. *Environ Pollut* 163:68–76.
69. Gerrard PM, St Louis VL. 2001. The effects of experimental reservoir creation on the bioaccumulation of methylmercury and reproductive success of tree swallows (*Tachycineta bicolor*). *Environ Sci Technol* 35:1329–1338.
70. Wolfe M, Norman D. 1998. Effects of waterborne mercury on terrestrial wildlife at Clear Lake: Evaluation and testing of a predictive model. *Environ Toxicol Chem* 17:214–227.
71. Vermeer K, Armstrong FAJ, Hatch DRM. 1973. Mercury in aquatic birds at Clay Lake, western Ontario. *J Wildl Manage* 37:58–61.
72. Custer CM, Custer TW, Warburton D, Hoffman DJ, Bickham JW, Matson CW. 2006. Trace element concentrations and bioindicator responses in tree swallows from northwestern Minnesota. *Environ Monit Assess* 118:247–266.
73. Custer TW, Dummer PM, Custer CM, Li AU, Warburton D, Melancon MJ, Hoffman DJ, Matson CW, Bickham JW. 2007. Water level management and contaminant exposure to tree swallows nesting on the upper Mississippi River. *Environ Monit Assess* 133:335–345.
74. Anderson DW, Suchanek TH, Eagles-Smith CA, Cahill TM Jr. 2008. Mercury residues and productivity in osprey and grebes from a mine-dominated ecosystem. *Ecol Appl* 18:A227–A238.
75. Henny CJ, Hill EF, Hoffman DJ, Spalding MG, Grove RA. 2002. Nineteenth century mercury: Hazard to wading birds and cormorants of the Carson River, Nevada. *Ecotoxicology* 11:213–231.
76. US Environmental Protection Agency. 1993. Wildlife exposure factors handbook, Vols 1 and 2. EPA 600/R-93/187a,b. Washington, DC.
77. Heinz GH. 1979. Methyl mercury: Reproductive and behavioral effects on three generations of mallard ducks. *J Wildl Manage* 43:394–401.
78. Tejning S. 1967. Biological effects of methyl mercury dicyandiamide–treated grain in the domestic fowl *Gallus gallus* L. *Oikos*(Suppl. 8):1–116.
79. Nagy KA. 2001. Food requirements of wild animals: Predictive equations for free-living mammals, reptiles, and birds. *Nutr Abstr Rev Ser Livestock Feeds Feeding* 71:21R–32R.
80. Kushlan JA. 1978. Feeding ecology of wading birds. In Sprunt A IV, Ogden JC, Winckler S, eds, *Wading Birds Research Report No. 7 of the National Audubon Society*. National Audubon Society, New York, NY, USA, pp 249–296.
81. Rodewald P, ed. 2016. The Birds of North America. Ithaca (NY): Cornell Laboratory of Ornithology. [cited 2016 August 1]. Available from: https://birdsna.org
82. Green JW. 2015. Data should not be normalized to the control for analysis. *Abstract*, 36th Annual Meeting, Society of Environmental Toxicology and Chemistry North America, Salt Lake City, UT, USA, 1–5 November.
83. R Core Team. 2016. *R: A Language and Environment for Statistical Computing*. R Foundation for Statistical Computing, Vienna, Austria.
84. Ritz C, Streibig JC. 2005. Bioassay analysis using R. *J Stat Softw* 12. DOI: 10.18637/jss.v012.i05.
85. Varian-Ramos CW, Swaddle JP, Cristol DA. 2014. Mercury reduces avian reproductive success and imposes selection: An experimental study with adult- or lifetime-exposure in zebra finch. *PLoS One* 9: e95674.
86. Eskeland B, Nafstad I. 1978. The modifying effect of multiple generation selection and dietary cadmium on methyl mercury toxicity in Japanese quail. *Arch Toxicol* 40:303–314.
87. Eskeland B, Gullvåg BM, Nafstad I. 1979. Quantitative studies of mercury and cadmium deposition in Japanese quail through multiple generations. *Acta Agric Scand* 29:113–118.
88. Heinz GH. 1974. Effects of low dietary levels of methyl mercury on mallard reproduction. *Bull Environ Contam Toxicol* 11:386–392.
89. Heinz GH. 1976. Methylmercury: Second-year feeding effects on mallard reproduction and duckling behavior. *J Wildl Manage* 40:82–90.
90. Heinz GH. 1976. Methylmercury: Second-generation reproductive and behavioral effects on mallard ducks. *J Wildl Manage* 40:710–715.
91. Heinz GH, Hoffman DJ. 1998. Methylmercury chloride and selenomethionine interactions on health and reproduction in mallards. *Environ Toxicol Chem* 17:139–145.
92. Heinz GH, Hoffman DJ, Klimstra JD, Stebbins KR. 2010. Enhanced reproduction in mallards fed a low level of methylmercury: An apparent case of hormesis. *Environ Toxicol Chem* 29:650–653.

93. He M, Wang WX. 2011. Factors affecting the bioaccessibility of methylmercury in several marine fish species. *J Agric Food Chem* 59:7155–7162.
94. Ralston NVC, Azenkeng A, Raymond LJ. 2012. Mercury-dependent inhibition of selenoenzymes and mercury toxicity. In Ceccatelli S, Aschner M, eds, *Methylmercury and Neurotoxicity*. Springer, New York, NY, USA, pp 91–99.
95. Peakall DB, Peakall ML. 1973. Effect of a polychlorinated biphenyl on the reproduction of artificially and naturally incubated dove eggs. *J Appl Ecol* 10:863–868.
96. El-Begearmi MM, Ganther HE, Sunde ML. 1982. Dietary interaction between methylmercury, selenium, arsenic, and sulfur amino acids in Japanese quail. *Poult Sci* 61:272–279.
97. US Environmental Protection Agency. 1995. Great Lakes water quality initiative criteria documents for the protection of wildlife, DDT, mercury, 2,3,7,8-TCDD, PCBs. EPA 820/B-95/008. Washington, DC.
98. Sample BE, Opresko DM, Suter GW II. 1996. Toxicological benchmarks for wildlife: 1996 revision. ES/ER/TN-86/R3. US Department of Energy, Oak Ridge National Laboratory, Oak Ridge, TN.
99. Environment Canada. 2002. Canadian tissue residue guidelines for the protection of wildlife consumers of aquatic biota: Methylmercury. Scientific supporting document. Ecosystem health: Science-based solutions. Report 1-4. National Guidelines and Standards Office, Environmental Quality Branch, Ottawa, Canada.
100. European Commission. 2005. Common implementation strategy for the Water Framework Directive. Environmental quality standards (EQS) substance data sheet priority substance no. 21, mercury and its compounds CAS No 7439-97-6. Final version. Brussels, Belgium.
101. Heinz GH, Hoffman DJ, Klimstra JD, Stebbins KR, Kondrad SL, Erwin CA. 2012. Hormesis associated with a low dose of methylmercury injected into mallard eggs. *Arch Environ Contam Toxicol* 62:141–144.
102. Varian-Ramos CW, Swaddle JP, Cristol DA. 2013. Familial differences in the effects of mercury on reproduction in zebra finches. *Environ Pollut* 182:316–323.
103. Leermakers M, Baeyens W, Quevauviller P, Horvat M. 2005. Mercury in environmental samples: Speciation, artifacts and validation. *Trends Anal Chem* 24:383–393.
104. Heinz GH, Locke LN. 1976. Brain lesions in mallard ducklings from parents fed methylmercury. *Avian Dis* 20:9–17.
105. Folland WR, Newsted JL, Fitzgerald SD, Fuchsman PC, Bradley PW, Kern J, Kannan K, Remington RE, Zwiernik MJ. 2016. Growth and reproductive effects from dietary exposure to Aroclor 1268 in mink (*Neovison vison*), a surrogate model for marine mammals. *Environ Toxicol Chem* 35:604–618.
106. Henny CJ, Grove RA, Bently VR. 2000. Effects of selenium, mercury, and boron on waterbird egg hatchability at Stillwater, Malheur, Seedskadee, Ouray, and Benton Lake National Wildlife Refuges and surrounding vicinities. National Irrigation Water Quality Program Information Report 5. Bureau of Reclamation, Denver, CO, USA.
107. Heinz GH, Hoffman DJ. 2003. Embryotoxic thresholds of mercury: Estimates from individual mallard eggs. *Arch Environ Contam Toxicol* 44:257–264.
108. Frederick P, Jayasena N. 2011. Altered pairing behaviour and reproductive success in white ibises exposed to environmentally relevant concentrations of methylmercury. *Proc Biol Sci* 278:1851–1857.
109. Newton I, Haas MB. 1988. Pollutants in merlin eggs and their effects on breeding. *British Birds* 81:258–269.
110. Jackson AK, Evers DC, Etterson MA, Condon AM, Folsom SB, Detweiler J, Schmerfeld J, Cristol DA. 2011. Mercury exposure affects the reproductive success of a free-living terrestrial songbird, the Carolina wren (*Thryothorus ludovicianus*). *Auk* 128:759–769.
111. Depew DC, Basu N, Burgess NM, Campbell LM, Evers DC, Grasman KA, Scheuhammer AM. 2012. Derivation of screening benchmarks for dietary methylmercury exposure for the common loon (*Gavia immer*): Rationale for use in ecological risk assessment. *Environ Toxicol Chem* 31:2399–2407.
112. Evers DC, Savoy LJ, DeSorbo CR, Yates DE, Hanson W, Taylor KM, Siegel LS, Cooley JH Jr, Bank MS, Major A, Munney K, Mower BF, Vogel HS, Schoch N, Pokras M, Goodale MW, Fair J. 2008. Adverse effects from environmental mercury loads on breeding common loons. *Ecotoxicology* 17:69–81.
113. Barr JF. 1986. Population dynamics of the common loon (*Gavia immer*) associated with mercury-contaminated waters in northwestern Ontario. Occasional Paper 56. Canadian Wildlife Service, Ottawa, ON, Canada.
114. Kenow KP, Meyer MW, Rossmann R, Gendron-Fitzpatrick A, Gray BR. 2011. Effects of injected methylmercury on the hatching of common loon (*Gavia immer*) eggs. *Ecotoxicology* 20:1684–1693.
115. Driscoll CT, Han Y-J, Chen CY, Evers DC, Lambert KF, Holsen TM, Kamman NC, Munson RK. 2007. Mercury contamination in forest and freshwater ecosystems in the northeastern United States. *BioScience* 57:17–28.
116. Merrill EH, Hartigan JJ, Meyer MW. 2005. Does prey biomass or mercury exposure affect loon chick survival in Wisconsin? *J Wildl Manage* 69:57–67.
117. Stafford CP, Haines TA. 2001. Mercury contamination and growth rate in two piscivore populations. *Environ Toxicol Chem* 20:2099–2101.
118. Kenow KP, Meyer MW, Rossmann R, Gray BR, Arts MT. 2015. Influence of in ovo mercury exposure, lake acidity, and other factors on common loon egg and chick quality in Wisconsin. *Environ Toxicol Chem* 34:1870–1880.
119. Schoch N, Glennon MJ, Evers DC, Duron M, Jackson AK, Driscoll CT, Ozard JW, Sauer AK. 2014. The impact of mercury exposure on the common loon (*Gavia immer*) population in the Adirondack Park, New Jersey, USA. *Waterbirds* 37(sp1):133–146.
120. Barr JF. 1996. Aspects of common loon (*Gavia immer*) feeding biology on its breeding ground. *Hydrobiologia* 321:119–144.
121. Champoux L, Masse DC, Evers D, Lane OP, Plante M, Timmermans STA. 2006. Assessment of mercury exposure and potential effects on common loons (*Gavia immer*) in Quebec. *Hydrobiologia* 567:263–274.
122. Heinz GH, Hoffman DJ, Klimstra JD, Stebbins KR. 2010. Intraperitoneal injections as a possible means of generating varied levels of methylmercury in the eggs of birds in field studies. *Environ Toxicol Chem* 29:1079–1083.
123. Brasso RL, Cristol DA. 2008. Effects of mercury exposure on the reproductive success of tree swallows (*Tachycineta bicolor*). *Ecotoxicology* 17:133–141.
124. Custer CM, Custer TW, Hill EF. 2007. Mercury exposure and effects on cavity-nesting birds from the Carson River, Nevada. *Arch Environ Contam Toxicol* 52:129–136.
125. Winder VL. 2012. Characterization of mercury and its risk in Nelson's, saltmarsh, and seaside sparrows. *PLoS One* 7:e44446.
126. Seewagen CL. 2013. Blood mercury levels and the stopover refueling performance of a long-distance migratory songbird. *Can J Zool* 91:41–45.
127. Townsend JM, Rimmer CC, Driscoll CT, McFarland KP, Inigo-Elias EE. 2013. Mercury concentrations in tropical resident and migrant songbirds on Hispaniola. *Ecotoxicology* 22:86–93.
128. Jackson A, Evers D. 2011. Mercury contamination and productivity in Carolina wrens nesting along the South River, Virginia, 2009–2010. Final report. BRI 2010-25. Prepared for US Fish and Wildlife Service, Gloucester, VA, by BioDiversity Research Institute, Gorham, ME, USA.
129. Thompson BC, Knadle GE, Brubaker DL, Brubaker KS. 2001. Nest success is not an adequate comparative estimate of avian reproduction. *J Field Ornithol* 72:527–536.
130. Ackerman JT, Herzog MP, Hartman CA, Isanhart J, Herring G, Vaughn S, Cavitt JF, Eagles-Smith CA, Browers H, Cline C, Vest J. 2015. Mercury and selenium contamination in waterbird eggs and risk to avian reproduction at Great Salt Lake, Utah. Open file report 2015-1020. US Department of the Interior, US Geological Survey, Reston, VA.
131. Robinson SA, Forbes MR, Hebert CE, Scheuhammer AM. 2011. Evidence for sex differences in mercury dynamics in double-crested cormorants. *Environ Sci Technol* 45:1213–1218.
132. Eagles-Smith CA, Ackerman JT, Yee J, Adelsbach TL. 2009. Mercury demethylation in waterbird livers: Dose–response thresholds and differences among species. *Environ Toxicol Chem* 28:568–577.
133. US Environmental Protection Agency. 2011. Recommended use of body weight 3/4 as the default method in derivation of the oral reference dose. EPA 100/R-11/0001. Washington DC.
134. Sharma V, McNeill JH. 2009. To scale or not to scale: The principles of dose extrapolation. *Br J Pharmacol* 157:907–921.
135. Huang Q, Riviere JE. 2014. The application of allometric scaling principles to predict pharmacokinetic parameters across species. *Expert Opin Drug Metab Toxicol* 10:1241–1253.
136. Hudson LN, Isaac NJB, Reuman DC. 2013. The relationship between body mass and field metabolic rate among individual birds and mammals. *J Anim Ecol* 82:1009–1020.

137. Lavin SR, Karasov WH. 2008. Allometry of paracellular absorption in birds. *Physiol Biochem Zool* 81:551–560.
138. Agency for Toxic Substances and Disease Registry. 1999. Toxicological profile for mercury. PB/99/142416. US Department of Health and Human Services, Public Health Service, Atlanta, GA.
139. Williams JB, Miller RA, Harper JM, Wiersma P. 2010. Functional linkages for the pace of life, life-history, and environment in birds. *Integr Comp Biol* 50:855–868.
140. Jimenez AG, Cooper-Mullin C, Calhoon EA, Williams JB. 2014. Physiological underpinnings associated with differences in pace of life and metabolic rate in north temperate and neotropical birds. *J Comp Physiol B* 184:545–561.
141. Hunter RP. 2010. Interspecies allometric scaling. In Cunningham F, Elliott J, Lees P, eds, *Handbook of Experimental Pharmacology*, Vol 199—Comparative and Veterinary Pharmacology. Springer-Verlag, Berlin, Germany, pp 139–157.
142. Sample BE, Fairbrother A, Kaiser A, Law S, Adams B. 2014. Sensitivity of ecological soil-screening levels for metals to exposure model parameterization and toxicity reference values. *Environ Toxicol Chem* 33:2386–2398.
143. Calatayud M, Devesa V, Virseda JR, Barberá R, Montoro R, Vélez D. 2012. Mercury and selenium in fish and shellfish: Occurrence, bioaccessibility and uptake by Caco-2 cells. *Food Chem Toxicol* 50:2696–2702.
144. Torres-Escribano S, Denis S, Blanquet-Diot S, Calatayud M, Barrios L, Vélez D, Alric M, Montoro R. 2011. Comparison of a static and a dynamic in vitro model to estimate the bioaccessibility of As, Cd, Pb and Hg from food reference materials *Fucus* sp. (IAEA-140/TM) and lobster hepatopancreas (TORT-2). *Sci Total Environ* 409:604–611.
145. Wang HS, Xu WF, Chen ZJ, Cheng Z, Ge LC, Man YB, Giesy JP, Du J, Wong CK, Wong MH. 2013. In vitro estimation of exposure of Hong Kong residents to mercury and methylmercury via consumption of market fishes. *J Hazard Mater* 248–249:387–393.
146. Berntssen MHG, Hylland K, Lundebye A-K, Julshamn K. 2004. Higher faecal excretion and lower tissue accumulation of mercury in Wistar rats from contaminated fish than from methylmercury chloride added to fish. *Food Chem Toxicol* 42:1359–1366.
147. Kaufman CA, Bennett JR, Koch I, Reimer KJ. 2007. Lead bioaccessibility in food web intermediates and the influence on ecological risk characterization. *Environ Sci Technol* 41:5902–5907.
148. Cuvin-Aralar MLA, Furness RW. 1991. Mercury and selenium interaction: A review. *Ecotoxicol Environ Saf* 21:348–364.
149. Yang D-Y, Chen Y-W, Gunn JM, Belzile N. 2008. Selenium and mercury in organisms: Interactions and mechanisms. *Environ Rev* 16:71–92.
150. Peterson SA, Ralston NVC, Peck DV, Van Sickle J, Robertson JD, Spate VL, Morris JS. 2009. How might selenium moderate the toxic effects of mercury in stream fish of the western US? *Environ Sci Technol* 43:3919–3925.
151. Harris HH, Pickering IJ, George GN. 2003. The chemical form of mercury in fish. *Science* 301:1203.
152. Magat WJ, Sell JL. 1981. Binding of methylmercury to ovalbumin as methylmercuric cysteine. *J Agric Food Chem* 29:543–547.
153. US Environmental Protection Agency. 2005. Guidance for developing ecological soil screening levels. OSWER Directive 9285.7-55. Washington, DC.
154. Fimreite N. 1970. Effects of methyl mercury treated feed on the mortality and growth of leghorn cockerels. *Can J Anim Sci* 50:387–389.
155. Fuchsman P, Henning M, Sorensen M, Brown L, Bock M, Beals C, Lyndall J, Magar V. 2016. Critical perspectives on mercury toxicity reference values for protection of fish. *Environ Toxicol Chem* 35:529–549.
156. Hope BK, Louch J. 2014. Pre-Anthropocene mercury residues in North American freshwater fish. *Integr Environ Assess Manage* 10:299–308.
157. Beckvar N, Dillon TM, Read LB. 2005. Approaches for linking whole-body fish tissue residues of mercury or DDT to biological effects thresholds. *Environ Toxicol Chem* 24:2094–2105.
158. Dentener F, Drevet J, Lamarque JF, Bey I, Eickhout B, Fiore AM, Hauglustaine D, Horowitz LW, Krol M, Kulshrestha UC, Lawrence M, Galy-Lacaux C, Rast S, Shindell D, Stevenson D, Van Noije T, Atherton C, Bell N, Bergman D, Butler T, Cofala J, Collins B, Doherty R, Ellingsen K, Galloway J, Gauss M, Montanaro V, Muller JF, Pitari G, Rodriguez J, Sanderson M, Solomon F, Strahan S, Schultz M, Sudo K, Szopa S, Wild O. 2006. Nitrogen and sulfur deposition on regional and global scales: A multimodel evaluation. *Global Biogeochem Cycles* 20:GB4003.
159. Selin NE, Jacob DJ, Yantosca RM, Strode S, Jaegle L, Sunderland EM. 2008. Global 3-D land–ocean–atmosphere model for mercury: Present-day versus preindustrial cycles and anthropogenic enrichment factors for deposition. *Global Biogeochem Cy* 22:GB2011.
160. Depew DC, Burgess NM, Campbell LM. 2013. Modelling mercury concentrations in prey fish: Derivation of a national-scale common indicator of dietary mercury exposure for piscivorous fish and wildlife. *Environ Pollut* 176:234–243.
161. Anthony RG, Miles AK, Ricca MA, Estes JA. 2007. Environmental contaminants in bald eagle eggs from the Aleutian Archipelago. *Environ Toxicol Chem* 26:1843–1855.
162. Ackerman JT, Takekawa JY, Eagles-Smith CA, Iverson SA. 2008. Mercury contamination and effects on survival of American avocet and black-necked stilt chicks in San Francisco Bay. *Ecotoxicology* 17:103–116.
163. French JB Jr, Bennett RS, Rossman R. 2010. Mercury in the blood and eggs of American kestrels fed methylmercury chloride. *Environ Toxicol Chem* 29:2206–2210.
164. Ou L, Varian-Ramos CW, Cristol DA. 2015. Effect of laying sequence on egg mercury in captive zebra finches: An interpretation considering individual variation. *Environ Toxicol Chem* 34:1787–1792.
165. Finley MT, Stendell RC. 1978. Survival and reproductive success of black ducks fed methyl mercury. *Environ Pollut* 16:51–64.
166. Heinz GH, Hoffman DJ, Klimstra JD, Stebbins KR. 2010. Predicting mercury concentrations in mallard eggs from mercury in the diet or blood of adult females and from duckling down feathers. *Environ Toxicol Chem* 29:389–392.
167. Henny CH, Kaiser JL, Packard HA, Grove RA, Taft MR. 2005. Assessing mercury exposure and effects to American dippers in headwater streams near mining sites. *Ecotoxicology* 14:709–725.
168. Suchanek TH, Eagles-Smith CA, Slotton DG, Harner EJ, Colwell AE, Anderson NL, Mullen LH, Flanders JR, Adam DP, McElroy KJ. 2008. Spatiotemporal trends in fish mercury from a mine-dominated ecosystem: Clear Lake, California. *Ecol Appl* 18(Suppl.): A177–A195.
169. Northam WT, Allison LA, Cristol DA. 2011. Using group-specific PCR to detect predation of mayflies (Ephemeroptera) by wolf spiders (Lycosidae) at a mercury-contaminated site. *Sci Total Environ* 416:225–231.
170. Cristol DA, Brasso RL, Condon AM, Fovargue RE, Friedman SL, Hallinger KK, Monroe AP, White AE. 2008. The movement of aquatic mercury through terrestrial food webs. *Science* 320:335.
171. Evers DC, Taylor KM, Major A, Taylor RJ, Poppenga RH, Scheuhammer AM. 2003. Common loon eggs as indicators of methylmercury availability in North America. *Ecotoxicology* 12:69–81.
172. Brasso RL, Abdel Latif MK, Cristol DA. 2010. Relationship between laying sequence and mercury concentration in tree swallow eggs. *Environ Toxicol Chem* 29:1155–1159.
173. Taylor CD, Cristol DA. 2015. Tissue mercury concentrations and survival of tree swallow embryos, nestlings and young adult females on a contaminated site. *Bull Environ Contam Toxicol* 95:459–464.
174. Hill EF, Henny CJ, Grove RA. 2008. Mercury and drought along the lower Carson River, Nevada: II. Snowy egret and black-crowned night-heron reproduction on Lahontan Reservoir, 1997–2006. *Ecotoxicology* 17:117–131.
175. DesGranges JL, Rodrigue J, Laperle M. 1998. Mercury accumulation and biomagnification in ospreys (*Pandion haliaetus*) in the James Bay and Hudson Bay regions of Quebec. *Arch Environ Contam Toxicol* 35:330–341.
176. DesGranges JL, Rodrigue J, Laperle M. 1999. Breeding success of osprey under high seasonal methylmercury exposure. In Lucotte M, Schetagne R, Thérien N, Langlois C, Tremblay A, eds, *Mercury in the Biogeochemical Cycle*. Springer-Verlag Berlin, Germany, pp 287–293.
177. King KA, Custer TW, Quinn JS. 1991. Effects of mercury, selenium, and organochlorine contaminants on reproduction of Forster's terns and black skimmers nesting in a contaminated bay. *Arch Environ Contam Toxicol* 20:32–40.
178. Ackerman JT, Eagles-Smith CA. 2009. Integrating toxicity risk in bird eggs and chicks: Using chick down feathers to estimate mercury concentrations in eggs. *Environ Sci Technol* 43:2166–2172.
179. Ackerman JT, Eagles-Smith CA, Takekawa JY, Demers SA, Adelsbach TL, Bluso JD, Miles AK, Warnock N, Suchanek TH, Schwarzbach SE. 2007. Mercury concentrations and space use of

pre-breeding American avocets and black-necked stilts in San Francisco Bay. *Sci Total Environ* 384:452–466.
180. Fimreite N. 1974. Mercury contamination of aquatic birds in northwestern Ontario. *J Wildl Manage* 38:120–131.
181. Yeardley RB Jr, Lazorchak JM, Paulsen SG. 1998. Elemental fish tissue contamination in northeastern US lakes: Evaluation of an approach to regional assessment. *Environ Toxicol Chem* 17:1875–1884.
182. Ontario Ministry of the Environment. 2011. Rationale for the development of soil and ground water standards for use at contaminated sites in Ontario. PIBS 7386e01. Standards Development Branch, Toronto, ON, Canada.

A Calculation of the Environmental Footprint of a Granular Activated Carbon Regeneration Facility

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ABSTRACT

The U.S. Environmental Protection Agency (EPA) Superfund Division is responsible for maintaining a high standard of environmental quality, and thus must deal with the environment impacts of its own remedial activities. The regeneration of granular activated carbon (GAC), a substance used to purify contaminated water, is one example of a remediation activity with substantial environmental impacts. The objective of my project is to calculate the environmental footprint of GAC regeneration at the Siemens Reactivation facility in Parker, Arizona. I calculated the electricity usage, natural gas usage, potable water usage, employee gasoline usage, and wastewater production using information from site diagrams, facility process maps, and literature searches. I converted these values into units of CO_2e, NO_x, SO_x, PM_{10}, and HAP using conversion values from the *EPA Methodology for Understanding and Reducing a Project's Environmental Footprint*. I found that the largest environmental impact resulted from natural gas consumption and electricity usage in the carbon regeneration building. The selection of context-dependent conversion factors greatly impacted the accuracy of my results. Using the results from my GAC environmental impact assessment, remedial project managers can more effectively apply green remediation principles to their projects.

KEYWORDS

remediation, carbon footprint, climate change, Environmental Protection Agency (EPA), Superfund

INTRODUCTION

The U.S. Environmental Protection Agency (EPA) is responsible for monitoring and enforcing a high standard of environmental quality, and thus must also regulate the environmental impacts of its own remedial activities (EPA 2011a). The EPA Superfund program, established in response to human-induced environmental disasters in the 1970s, initiates and executes cleanup of abandoned hazardous waste sites, termed "Superfund" sites. The multistep Superfund cleanup process includes conducting rigorous site assessments, designing specific remediation strategies, and constructing contaminant profiles (EPA 2011b).

Remedial activities also have their own negative environmental impacts. The Superfund Program has acknowledged the potential environmental impact of its operations and as a result has developed a methodology to quantify the impacts of remediation projects and processes. This method outlines a process to estimate environmental impacts of specific remediation activities in all steps of the Superfund cleanup process (EPA 2012). The methodology investigates the extent of impacts associated with energy usage, water usage, material inputs, and waste discharge (ibid.). Superfund projects can last decades due to the complexity of projects and the EPA goal of sustained environmental protection in remediated sites (EPA 2011b). Consequently, these long-term cleanup projects can have substantial long-term environmental impacts (ibid.). For example, the Iron Mountain Mine cleanup project has cost nearly USD 55.5 million and has altered natural waterway trajectories to facilitate contaminant management (Region 9: Superfund 2011). EPA diverted streams loaded with heavy metals from the mine site to a water treatment plant. This diversion of water impacted the benthic invertebrate ecology and water quality of nearby riparian ecosystems (EPA 2004). These impacts were a direct result of the EPA-initiated remediation activities. The environmental footprint calculator used to estimate these and other impacts is currently being developed (Scheuermann, personal communication). Due to the novelty of the methodology and calculator, environmental impact values of many common remediation strategies incorporated in the footprint calculator are incomplete.

The regeneration of granular activated carbon (GAC) is one example of a Superfund site remediation activity whose calculated environmental footprint is incomplete. Activated carbon, a porous carbon-rich material, is used to filter harmful volatile organic compounds (VOCs) from contaminated water (Cannon et al. 1994). It has enormous adsorptive potential because it has the

largest surface area to mass ratio of any known substance (Mohan and Singh 2005). When contaminated water is poured into a matrix of GAC, the contaminants are attracted to the GAC's large surface area and are captured in the matrix (ibid.). Activated carbon is produced by heating various materials like coal, coconut shells, and bone to temperatures of 1000 °C (Mohan and Singh 2005, Bayer 2005). After use in water treatment, GAC can be regenerated through exposure to temperatures up to 800 °C in the presence of a mildly oxidative atmosphere (provided by steam and/or carbon dioxide). The heat and oxidative conditions vaporize the VOCs, which may be vented to the atmosphere in low concentrations (San Miguel et al. 2001).

The regeneration of GAC plays an important role in decreasing the demand for creation of virgin, or previously unused, GAC (San Miguel et al. 2001). This recycling process has many ecological benefits such as reducing the need for new GAC, but the recycling process could possibly be inefficient and more polluting than creating new GAC. The comparison between the environmental impacts of new GAC and recycled GAC is crucial to choosing an alternative that best promotes environmental sustainability. A preliminary environmental footprint of GAC regeneration has already been calculated, but it only quantifies electricity usage, natural gas usage, water usage, and wastewater discharged, and does not account for many resource inputs of machines used in the regeneration process (Scheuermann, personal communication). Thus, there is a need to improve the estimated environmental footprint of the GAC regeneration process to better reflect all of its consequences.

The objective of my project is to refine the current calculations of the environmental footprint of GAC regeneration to provide a more accurate environmental assessment tool. This objective will help answer the broader research question of how ecologically sustainable remediation methods can be implemented in Superfund site remedy decision models. To accomplish this research objective, I will recalculate the results from the existing environmental impact analysis to double-check previously calculated values and to include categories that are inclusive of different emission categories. I will compile my results and present them to the EPA Superfund Division.

BACKGROUND

The Siemens Water Technologies Corporation Parker Reactivation Facility in Parker, Arizona reactivates spent carbon using a thermal regeneration process: spent GAC is heated in a reactivation furnace, vaporizing the contaminants on the carbon. These contaminants are filtered from the furnace exhaust and vented to the atmosphere at regulated levels (Siemens 2007). The facility processes both vapor phase and liquid phase carbon with and without chlorinated contaminants. This distinction is important because different types of spent GAC have different resource consumption requirements (ibid.).

In addition to the carbon regeneration facility, the Siemens facility has on-site support buildings including a carbon product warehouse, a drum storage warehouse, and administrative offices (ibid.). Activities that support the carbon regeneration facility are emissions monitoring, on-site and off-site wastewater treatment, employee transportation, and laboratory analysis (to determine the contaminant composition).

The facility is currently undergoing a permitting process and has released a permit application that includes information about the layout and specifications of their machines and buildings (Siemens 2007). This permit application was a major source of information for my study.

METHODS

I separated the environmental impacts into six components: (1) electricity impacts, (2) natural gas impacts, (3) water impacts, (4) transportation impacts, (5) laboratory analysis, and (6) treatment chemicals. I calculated CO_2 emissions, NO_x emissions, SO_x emissions, PM_{10} emissions, and hazardous air pollutant (HAP) emissions for each component. I used Excel spreadsheets to organize my data.

General assumptions

Data in the process maps from the Siemens permit application was separated by carbon phase (vapor versus liquid) and carbon chlorination (non-chlorinated versus chlorinated). I

assumed a breakdown of 25% liquid phase non-chlorinated carbon, 25% liquid phase chlorinated carbon, 25% vapor phase non-chlorinated carbon, and 25% vapor phase chlorinated carbon (Scheuermann, personal communication).

I applied a 0.9 capacity factor to all processes in the regeneration building by multiplying final spent carbon and resource consumption estimates by 0.9 (Scheuermann, personal communication). This capacity factor accounts for downtime due to equipment maintenance and holidays. The 0.9 capacity factor was not applied to warehouse/office electricity and water consumption, transportation, or lab analysis - I incorporated system downtime for these activities using other methods.

I assumed 100% of energy consumption in warehouses and office buildings originated from grid electricity and not natural gas (Scheuermann, personal communication).

I worked in collaboration with EPA employees to assign reasonable assumptions whenever data was lacking.

Spent carbon data collection

I found the rate of spent carbon processing (in lb/hr) from process maps in the permit application (Siemens 2007). I converted this value into lb/year by multiplying by 24 hr/day and 365 days/year.

(1a) Electricity usage data collection and analysis

Wet electrostatic precipitator (WESP)

I found the power requirements (in kVA, kilo Volt Ampere) of the Clean Gas Systems (CGS) WESP from the permit application (Siemens 2007). I assumed the apparent power (VA) equaled real power (watts) and used a 1:1 conversion between kVA and kW. The listed power requirements were for a 7200 actual cubic feet per minute (acfm) WESP, while the facility's actual exhaust flow rate was 6717 acfm (this value was collected from the process maps). I prorated the power consumption by exhaust rate to calculate the actual power consumption. I

then multiplied the power consumption (in kW) by 8760 hr/year to calculate the annual electricity demand (in kWh).

Induced draft (ID) fan

I found the power requirements (in brake horsepower, bhp) of the Barron Industries Induced Draft (ID) fan from the permit application (Siemens 2007). I prorated the power requirements according to the actual exhaust flow rate (8039 acfm versus the 8420 acfm listed in the permit ID fan performance conditions) and applied a 90% motor efficiency to calculate the facility's ID fan power requirements (Scheuermann, personal communication). I converted the power requirements from bhp to kW (using a conversion factor of 746 watts/bhp, EPA 2012) and multiplied by 8760 hr/yr to calculate the annual energy consumption in kWh.

On-site wastewater treatment plant (WWTP)

I found the wastewater flow rate (in gal/min) to the on-site WWTP in the permit application process maps (Siemens 2007). I multiplied the flow rate by one half of the estimated electricity demand (in kWh/gal) of a municipal wastewater treatment plant (EPA 2010) to calculate the annual electricity demand (in kWh). I assumed the Siemens on-site WWTP would have half the electricity demand of a municipal WWTP because it is a pre-treatment plant for treating wastewaters before discharge to the local publicly owned treatment works (POTW) and would therefore have a lower power requirement (Scheuermann, personal communication).

Continuous emissions monitoring system (CEMS)

I found the power requirements (in Voltage-Amps, VA) of the four emissions monitoring devices in the permit application (Siemens 2007) and from device manuals (Siemens 2001). I assumed apparent power (VA) equaled real power (watts) and applied a 1:1 VA:watt conversion factor to calculate power requirements of the devices (in watts). I summed the power requirements of all four devices to calculate the total CEMS power requirement and divided by

1000 to calculate power in kW. Finally, I multiplied by 8760 hr/yr to calculate the annual electricity demand (in kWh).

Drum and carbon product storage warehouses

I found the dimensions of the office buildings in the permit application (Siemens 2007) and multiplied the length by the width to calculate the total area (in ft^2). I then multiplied this area by a conversion factor of 5.38 kWh/ft^2. I calculated this conversion factor by dividing a conversion factor from the literature (in units of USD/ft^2 annually spent on energy, E Source 2007) by the 2007 price of electricity for industrial customers (EIA 2011). I reduced this final value by 50% because the warehouses at the Siemens facility are not intensively heated or cooled (Scheuermann, personal communication).

Administrative offices

I found the dimensions of the office buildings in the permit application (Siemens 2007) and multiplied the length by the width to calculate the total area (in ft^2). I calculated a energy density conversion factor (in kwh/ft^2) from E Source 2006: "office buildings in the U.S. use an average of 17 kilowatt-hours (kWh) of electricity and 32 cubic feet of natural gas per square foot annually." I assumed 100% of the facility's energy requirements were supplied by electricity (Scheuermann, personal communication) and added the cited 32 ft^3 natural gas/ft^2 to the 17 kWh/ft^2. I converted "32 ft^3 of natural gas" into 9 kWh/ft^2 by multiplying by 1,000 Btu/ft^3 natural gas and 3412 Btu/kWh (APS 2012). I multiplied the area by this conversion factor (26 kWh/ft^2) to calculate the annual energy consumption of the office buildings.

Miscellaneous fans, pumps, and motors

Carbon regeneration equipment not included in the above calculations was powered by fans, pumps, and motors. I quantified their electricity consumption by calculating the electricity consumption of all fans (excepting the ID fan), pumps, and motors.

I summed all the fans, pumps, and motors identified from process diagrams in the permit application (Siemens 2007). I assumed fans, pumps, and motors all operated at 5 hp (Scheuermann, personal communication). I converted 5 hp into kWh/yr by multiplying by 8760 hr/yr and 0.746 kW/hp (EPA 2012). I multiplied the total number of items by the per unit energy consumption (in kWh/yr) to calculate the estimated annual electricity usage.

(1b) Electricity emissions conversion

Energy composition

I found the electricity fuel blend supplied to the facility (in terms of percentage of power mix – e.g. % coal, % natural gas, % renewable energy) (APS 2009). I then converted the resource mix to footprint conversion factors by multiplying total emissions (in lb/ MWh) (EPA 2012) by the fraction of power mix. I summed all of these emissions by type of emission (CO_2e, NO_x, PM_{10}, etc.) to calculate the emissions per kWh of electricity supplied in this region of Arizona.

Electricity generation impact

I summed the electricity consumption (in kWh) of all activities listed above to calculate the annual electricity consumption. I converted kWh into MWh by multiplying by MWh/1000 kWh and multiplied this total consumption by the emissions conversion factors calculated in the previous section titled “Energy composition” to calculate emissions (in lb/yr) of CO_2, NO_x, SO_x, PM_{10}, and HAP.

(2a) Natural gas data collection and analysis

Reactivation furnace and afterburner burners

I found the natural gas flow rate (in standard cubic feet per minute, scfm) into the reactivation furnace and the afterburner in the Siemens permit application (Siemens 2007). I converted scfm into annual usage by multiplying by 60min/hr and 8760 hr/yr.

For comparison purposes, I also calculated burner annual natural gas consumption using manufacturer's information from the permit application (Siemens 2007). The permit application provided the number of burners in the furnace and afterburner as well as the rate of natural gas consumption per burner in scf/hr. I calculated the annual natural gas usage by multiplying the number of burners by the per burner rate of natural gas consumption and by 8760 hr/yr.

Small boiler

The natural gas flow rate of the small boiler was not provided in the process maps. However, the steam production rate (in lb/hr) of the boiler was given. I used tables that quantify heat quantities and temperature/pressure relationships, steam tables, to determine the energy (in Btu/lb) required to heat the steam (Spirax 2012). I converted the steam production rate into annual natural gas consumption by multiplying the steam production rate (in lb/hr) by the energy requirement (in Btu/lb), an assumed boiler efficiency (Scheuermann, personal communication), 8760 hr/yr, and the energy content of natural gas (Btu/scf) (APS 2012).

(2b) Natural gas emissions conversion

Natural gas impact

I summed the natural gas consumption of the burners and boilers to calculate the annual natural gas usage of the facility (in scf). I multiplied this quantity by emissions conversion factors (in lb/scf) from the EPA methodology (EPA 2012) to calculate emissions of CO_2, NO_x, SO_x, PM_{10}, and HAP. I applied conversion factors for both natural gas production and natural gas usage.

(3a) Water usage data collection and analysis

Potable water usage

Carbon regeneration system. I summed the flow rates (in gal/min) of all consumers of potable water in the facility (Siemens 2007). I converted this quantity into gal/yr by multiplying by 60 min/hr and 8760 hr/yr.

Other industrial uses. I found the weekly truck traffic in the permit application (Siemens 2007). I assumed that 2 trucks/day carried GAC in bulk and 1 truck/day carried GAC in drums. I assumed each truck carried 30 drums. I assumed truck wash-down required 1000 gallons per truck and drum wash-down required 10 gallons per drum. I multiplied the number of bulk trucks per week by 260 working days/yr to calculate annual truck traffic and multiplied by 1000 gal/truck to calculate the annual water usage for truck wash-down. I converted one drum truck/day into annual drum truck wash-down water consumption by multiplying by 30 drums/truck, 260 working days/yr, and 10 gal/drum. I estimated water consumption of general maintenance to be 500 gal/day. I multiplied this quantity by 260 working days/yr to calculate annual water usage due to general maintenance. I summed the water consumption from drum wash-down, truck wash-down, and general maintenance to calculate the annual water usage from other industrial uses. All of these assumptions were reasonable estimates made in collaboration with Karen Scheuermann of EPA Region 9.

Administrative offices. I found the dimensions of administrative office space in the permit application (Siemens 2007). I multiplied the length by the width of the buildings to calculate the total area (in ft^2). I multiplied the area by the average annual corporate water usage (m^3 water/m^2 office space) to calculate the annual water usage in m^3/yr (Seneviratne 2007). I then multiplied this quantity by 264 gal/m^3 to calculate the annual water usage in gal/yr.

Wastewater production

Carbon regeneration system. I found the wastewater flow rate (in gal/min) to the off-site POTW in the facility process maps (Siemens 2007). I multiplied by 60 min/hour and by 8760 hr/yr to calculate the annual discharge to the POTW.

Administrative offices. I assumed water loss in office water use activities was negligible and that wastewater produced through office use was the same as potable water domestic use (Scheuermann, personal communication).

(3b) Water emissions conversion

Potable water production impact

I summed water usage of the carbon regeneration system, other industrial uses, and office use to calculate the total annual water usage in the facility (in gal). I divided by 1000 to convert to thousands of gallons (galx1000). I then multiplied this quantity by emissions conversion factors (in lb/galx1000) from the EPA methodology (EPA 2012) to calculate annual emissions of CO_2, NO_x, SO_x, PM_{10}, and HAP.

Off-site wastewater treatment impact

I summed wastewater production of the carbon regeneration system and office use to calculate the total annual water usage in the facility (in gal). Wastewater produced from "other industrial uses" flows into sumps that lead to the carbon regeneration system and would thus be included in wastewater calculations. I divided this quantity by 1000 to convert to galx1000. I then multiplied this quantity by emissions conversion factors (in lb/galx1000) from the EPA methodology (EPA 2012) to calculate annual emissions of CO_2, NO_x, SO_x, and PM_{10}. HAP emission conversion factors were unavailable for off-site wastewater treatment.

(4a) Transportation data collection and analysis

I found the number of facility employees in the permit application (Siemens 2007). I assumed half of the employees lived in Parker, AZ, and half of the employees lived in Lake Havasu, AZ, the nearest large city (Scheuermann, personal communication). I used Google maps to estimate the distance from the center of the two cities to the location of the facility (Google

2012). I averaged the two distances to calculate the average employee distance to the facility (in miles). I converted this quantity to gallons gasoline consumed per year by multiplying average employee distance to facility (mi) by number of employees and dividing by the average fuel efficiency of a passenger car (EPA 2012).

(4b) Transportation emissions conversion

I multiplied this quantity by emissions conversion factors (in lb/gal gasoline) from the EPA methodology (EPA 2012) to calculate emissions of CO_2, NO_x, SO_x, PM_{10}, and HAP. I applied conversion factors for both gasoline production and gasoline usage.

(5a) Laboratory analysis data collection and analysis

I assumed 100 facility clients per year require a set laboratory analyses. I assumed a set of laboratory analyses included metals analysis (USD 150/analysis), VOC analysis (USD 50/analysis), semi-volatile organic compound (SVOC) analysis (USD 125/analysis), general chemistry analysis (USD 150/analysis), and an analysis customized to the type of spent carbon (USD 150/analysis). I summed the costs of the five analyses to calculate the cost of a set of analyses. I multiplied this quantity by 100 customers/year to calculate the annual lab analysis cost. All assumptions and lab analysis costs were reasonable estimates made in collaboration with Karen Scheuermann of EPA Region 9.

(5b) Laboratory analysis emissions conversion

I multiplied the annual lab analysis cost by emissions conversion factors (in lb/USD) from the EPA methodology (EPA 2012) to calculate emissions of CO_2, NO_x, SO_x, PM_{10}, and HAP.

(6a) Treatment chemicals data collection and analysis

I found the caustic (sodium hydroxide (NaOH)) input rate (lb/hr) in the Siemens permit application (Siemens 2007). I multiplied this quantity by 8760 hr/yr to calculate the annual NaOH input (in lb).

(6b) Treatment chemicals emissions conversion

I multiplied the annual NaOH input by emissions conversion factors (in lb out/lb in) from the EPA methodology (EPA 2012) to calculate emissions of CO_2, NO_x, SO_x, PM_{10}, and HAP.

Total footprint calculation of recycled and virgin GAC

I summed all emissions for electricity generation, natural gas production, natural gas usage, potable water production, off-site wastewater treatment, gasoline production, gasoline usage, lab analysis, and NaOH production to calculate the facility's annual emissions of CO_2, NO_x, SO_x, PM_{10}, and HAP. I divided these emission values (in lb/year) by the annual amount of spent carbon processed (in lb/year) to calculate the pounds of emissions per pound of spent carbon.

I found the annual emissions of CO_2, NO_x, SO_x, PM_{10}, and HAP from generating virgin GAC in the EPA methodology (EPA 2012).

RESULTS

Overall GAC Regeneration Footprint and Comparison to Virgin GAC Production

Per pound of spent carbon processed, the Siemens carbon regeneration facility emitted 0.70 pounds of CO_2, 8.1×10^{-4} pounds of NO_x, 5.7×10^{-4} pounds of SO_x, 6.0×10^{-5} pounds of PM_{10}, and 1.6×10^{-5} pounds of HAP (Table 1). Producing one pound of virgin GAC emitted 8.5 pounds of CO_2, 0.014 pounds of NO_x, 0.034 pounds of SO_x, 0.00078 pounds of PM_{10}, and 0.0012 pounds of HAP (Table 2). Figure 1 compares the emissions of regenerating GAC to emissions of producing virgin GAC.

Natural gas usage and production resulted in the largest CO_2 emissions, comprising 85% of the total CO_2 footprint (Figure 2).

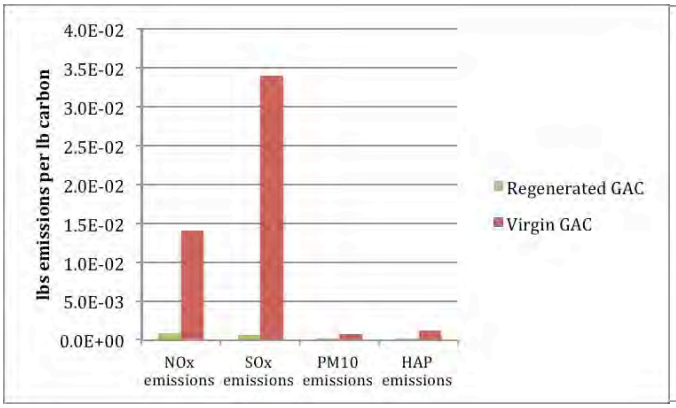

Fig. 1a. Emissions of recycled and virgin GAC.

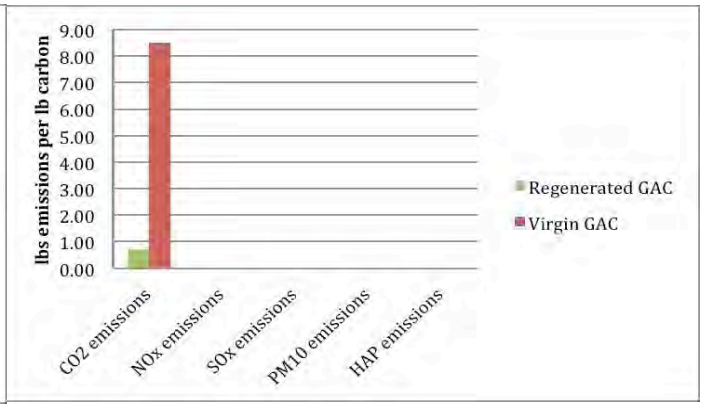

Fig 1b. Enlargement of NO_x, SO_x, PM_{10}, and HAP Emissions.

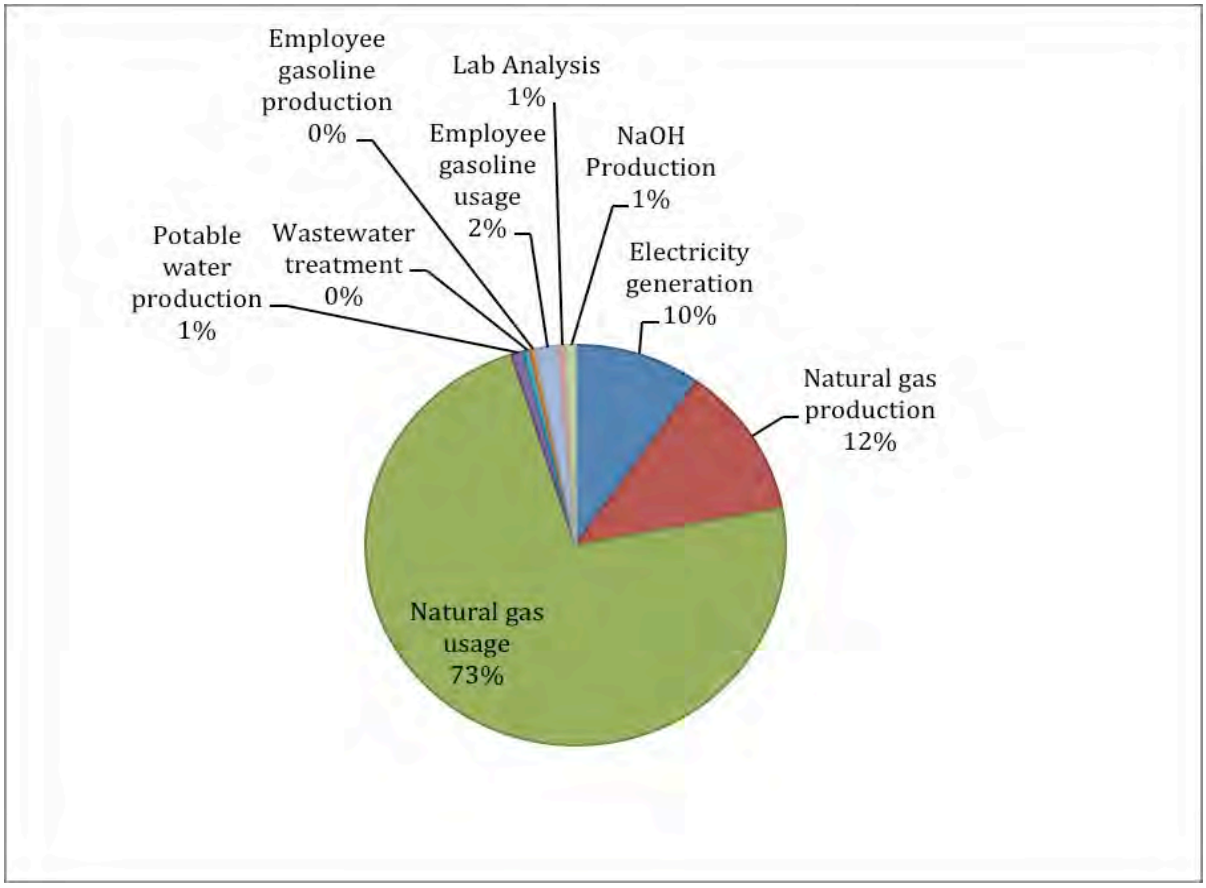

Fig. 2. CO_2 emissions breakdown by activity. 0% represents <0.1%.

Table 1. GAC regeneration footprint.

Activity	Quantity		Annual CO_2 emissions (lb)	Annual NO_x emissions (lb)	Annual SO_x emissions (lb)	Annual PM_{10} emissions (lb)	Annual HAP emissions (lb)
Electricity generation	883	MWh	1,094,193	2321	5038	53	228
Natural gas production	62,667	cu.ft.x1000	1,378,683	2319	2883	45	3.8
Natural gas usage	62,667	cu.ft.x1000	8,209,428	6267	3.9	476	5.3
Potable water production	20,073	galx1000	100,363	195	118	321	0.3
Wastewater treatment	14,182	galx1000	62,399	227	213	NP	NP
Employee gasoline production	10,010	gal	44,044	80	190	5.2	1.6
Employee gasoline usage	10,010	gal	196,196	1101	45	5.4	0.4
Lab Analysis	62,500	USD	62,500	300	225	25.0	8.1
NaOH Production	51,187	lb	87,018	154	333	31.2	0.8
Total emissions (lb)			11,234,824	12,963	9,049	963	249
Pounds emissions per pound of spent carbon (lb)			0.70	8.1E-04	5.7E-04	6.0E-05	1.6E-05

NP - Not Provided

Table 2. Virgin GAC footprint (for comparison).

	CO_2	NO_x	SO_x	PM_{10}	HAP
Pounds emissions per pound of virgin GAC (lb)	8.5	0.014	0.034	0.00078	0.0012

Electricity Consumption Breakdown and Impacts

Annually, the WESP consumed 78,840 kWh, the ID fan consumed 551,880 kWh, the WWTP consumed 4,598 kWh, the CEMS consumed 18,567 kWh, the drum storage warehouse consumed 77,538 kWh, the carbon product storage warehouse consumed 34,462 kWh, the administrative offices consumed 116,064 kWh, and the fans/pumps/motors consumed 1,176 kWh (Table 3). The largest electricity consumer was the ID fan, which comprised 62% of the total energy usage. The next largest consumers were the administrative offices (13%), the warehouses (13% combined), and the WESP (9%) (Figure 3).

Table 3. Electricity consumption.

Item	Annual electricity usage (kWh)
Wet Electrostatic Precipitator (WESP	78840
Induced Draft (ID) Fan	551880
Wastewater Treatment Plant (WWTP)	4598
Continuous Emissions Monitoring System (CEMS)	18567
Drum Storage Warehouse	77538
Carbon Product Storage Warehouse	34462
Administrative Offices	116064
Fans, Pumps, Motors	1176
Total:	883126

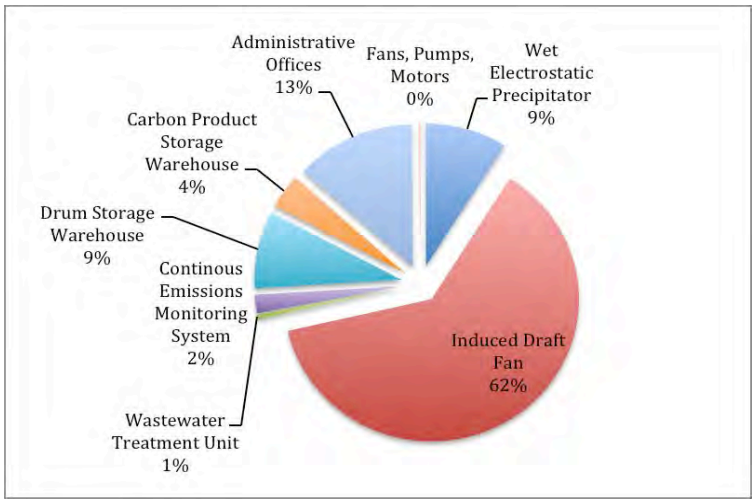

Fig. 3. Electricity consumption by activity. 0% represents <0.2%.

Natural Gas Consumption Breakdown and Impacts

Annually, the burners in the reactivation furnace consumed 20,577,000 ft^3 of natural gas, the small boiler consumed 7,440,000 ft^3 of natural gas, and the burners in the afterburner consumed 34,650,000 ft^3 of natural gas (Table 4). The largest natural gas consumer was the afterburner, which accounted for 55% of all consumption (Figure 4).

Table 4. Natural gas consumption.

Item	Annual natural gas usage (ft^3 x 1000)
Burners in Furnace	20577
Small Boiler	7440
Burners in Afterburner	34650
Total:	62667

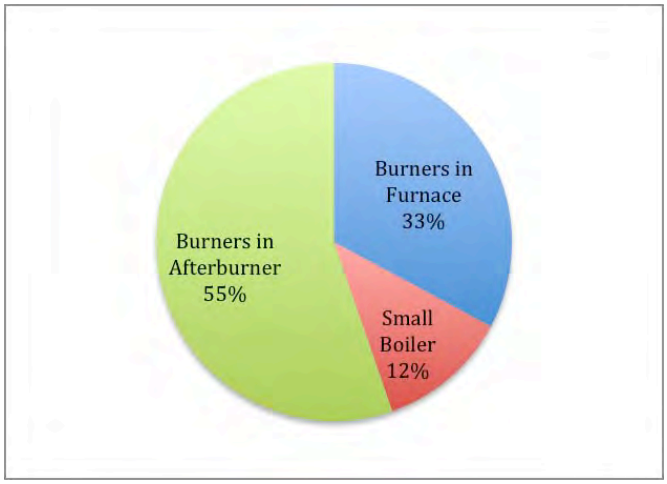

Fig. 4. Natural gas consumption by activity.

Water Consumption Breakdown and Impacts

Potable water

Annually, the carbon regeneration system consumed 19,108,000 gallons of water, other industrial site uses consumed 781,000 gallons of water, and administrative offices consumed 184,000 gallons of water (Table 5). The carbon regeneration system consumed the most water and accounted for 95% of the water consumption (Figure 5).

Table 5. Potable water usage.

Item	Annual flow rate (galx1000)
Carbon Regeneration System	19108
Other Industrial Site Uses	781
Administrative Offices	184
Total:	20073

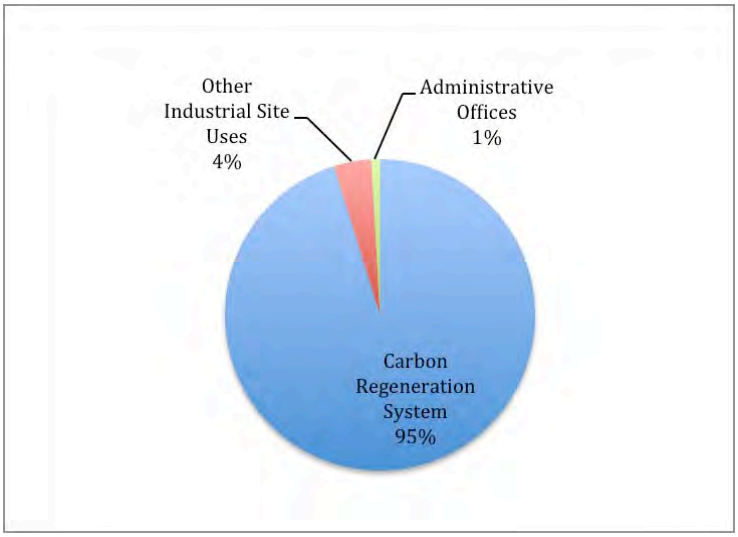

Fig. 5. Potable water consumption by activity.

Wastewater

Annually, the carbon regeneration facility produced 13,998,000 gallons of wastewater and administrative uses produced 184,000 gallons of wastewater (Table 6). The largest producer was the carbon regeneration facility, which accounted for 99% of the wastewater production (Figure 6).

Table 6. Water discharged to POTW.

Item	Annual flow rate (galx1000)
Carbon Regeneration Facility	13998
Administrative Offices	184
Total:	14182

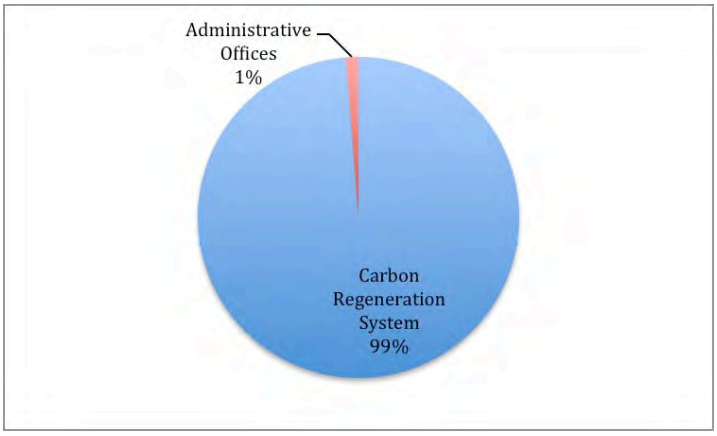

Fig. 6. Wastewater production by activity.

Transportation, Lab Analysis, and NaOH Breakdown and Impacts

Annually, employee transportation consumed 10,010 gallons of gasoline, laboratory analyses cost USD 62,500, and the regeneration facility consumed 51,187 lb of NaOH (Table 7). The units of these values are not comparable.

Table 7. Transportation, lab analyses, treatment chemicals.

Item	Amount	Unit
Transportation	10010	gal gasoline
Laboratory analyses	62500	USD spent
Treatment chemicals	51,187	lb NaOH

DISCUSSION

I found that the majority of the carbon footprint of the Siemens Reactivation facility resulted from natural gas usage and electricity usage in the carbon regeneration building. Because the Siemens facility has direct control over the operation of the carbon regeneration facility, there is great potential to reduce environmental impacts through efficiency measures. The choice of conversion values I used from the literature had the potential to change my calculated results greatly. When I reviewed my methods, I found that values for the same environmental impact that were calculated using two different estimation methods differed greatly, causing me to doubt the validity of derived values.

Electricity Usage

Machines in the regeneration building were the largest electricity consumers in the Siemens Reactivation facility. This pattern follows the national trend – 23 percent of electricity consumed in the United States is from industrial motor-driven systems (Consortium for Energy Efficiency (CEE) 2009).

The Induced Draft fan was the largest consumer of electricity in the facility, accounting for 62% of electricity consumption. Increasing the efficiency of the ID fan by purchasing a more efficient fan or optimizing its control system has the greatest potential for reducing electricity consumption. The ID fan pulls exhaust from the wet electrostatic precipitator through the air pollution control system to the stack that vents to the atmosphere. The fan is the largest consumer of energy and optimizing its control system can potentially reduce its electricity consumption by 40% (Mandi 2008). Another study found that incorporating more efficient motor systems like those in fans has the potential to decrease motor system demand by 11 – 18 percent (CEE 2009). Nationwide, this would result in emissions reductions of 15-26 million metric tons of carbon per year (ibid.).

Natural Gas Consumption

Natural gas consumption in the regeneration facility contributed to 73% of the aggregated carbon dioxide emissions. Industrial activities account for 33% of natural gas consumption nationally and 6% of natural gas consumption in Arizona (EIA 2012). Because industrial facilities comprise a substantial proportion of national natural gas consumption, reducing facility natural gas consumption has the potential to affect a large portion of national natural gas demand.

The cited natural gas consumption values underestimate the fraction of industry natural gas usage because they do not account for electricity generation. National electricity generation environmental impacts are primarily attributed to large users of electricity such as industrial facilities. Accounting for electricity generation, industrial activities in Arizona consume substantially more natural gas than the cited 6%. 68% of Arizona natural gas consumption is from electricity generation (ibid.) and industrial sources consume 16% of electricity in Arizona (EIA 2011). Multiplying 68% by 16% and adding this quantity to 6% increases the Arizona proportion of industrial natural gas consumption to 17%.

In part 2a of my analysis, I calculated burner natural gas consumption using two different methods for comparison purposes. The burner natural gas usage calculated from manufacturer's information sheets was roughly three times as high as the flow rate calculated from the process diagrams (Appendix A). The difference between these two estimates indicates that there are inconsistencies in the methods that I used. One source of error could have originated from the assumption that the burners work at 90% capacity, a rough estimate from an EPA employee (Scheuermann, personal communication). This 90% capacity factor is assumed for the entire facility.

Water Usage

I found that carbon impacts associated with water consumption were more than one order of magnitude smaller than electricity and natural gas impacts. Because the magnitude of water consumption impacts at the facility is small compared to impacts from electricity and natural gas usage, water efficiency measures will have a small effect on the overall

environmental impact. However, implementing water efficiency measures would have a small, but favorable impact on the environmental footprint. A study conducted by the City of San Jose examined 15 industrial facilities that have implemented water efficiency measures. These facilities were able to reduce their water use by 25% to 90% and most were able pay back the initial costs of their conservation measures in less than one year (CA DWR 1994).

Lack of data from the facility resulted in imprecise water usage calculations. The permit application did not quantify many of the carbon regeneration system water flows (e.g. to the top of the packed bed scrubber, to the top of the Venturi scrubber, to the cooling tower) and many on-site water consuming activities were implied but not explicitly listed in the application (e.g. carbon drum wash-down, truck wash down, general maintenance) (Siemens 2007). These values were estimated with back of the envelope calculations and are the least supported by published data.

Overall Environmental Impact Calculations

Industrial and commercial activities account for approximately two-thirds of energy usage in the U.S (McLean-Conner 2009). Reductions in overall environmental impact in facilities like the Siemens carbon regeneration facility would have a substantial impact on national electricity consumption.

One assumption that affected both the electricity consumption and the natural gas consumption was the assumption that 100% of building energy came from electricity and 0% of building energy originated from natural gas (E Source 2007). Modifying this assumption would have a significant impact on the aggregated carbon dioxide emissions. A larger proportion of electricity in the energy composition would lead to substantially higher carbon dioxide emissions, as the process of producing electricity is more carbon-intensive (Deru 2007, EGRID 2007).

Methods Assessment

The original footprint only included CO_2 emissions. My new calculation also included NO_x emissions, SO_x emissions, PM_{10} emissions, and HAP emissions. Table 8 shows the results

of the previous study compared to my study (Scheuermann 2011). The new carbon footprint of regenerating GAC is larger (0.70lb CO_2 versus 0.57lb CO_2), which could indicate that the new calculation included carbon emissions that were not previously quantified. Table 9 shows the items quantified in my study versus the previous study.

Table 8. Carbon emissions results of previous and new footprint calculations. NO_x emissions, SO_x emissions, PM_{10} emissions, and HAP emissions were not quantified in the previous calculation.

	Quantity		Units	Annual CO2 Emissions (lb)	
	Previous Calculation	**New Calculation**		**Previous Calculation**	**New Calculation**
Electricity Usage	660	883	MWh	1,016,757	1,094,193
Natural Gas Usage	52,667	62,667	cu.ft.x1000	6,425,369	1,378,683
Water Usage	16,680	20,073	galx1000	83,399	100,363
Wastewater Discharged	14,182	14,182	galx1000	62,399	62,399
Total Emissions (lb)				7,587,925	2,635,638
Pounds emissions per pound of spent carbon (lb)				0.57	0.70

Table 9. Items quantified in original and new environmental footprint. A checkmark indicates the analysis was completed for that item in that calculation.

Resource type	Item	Original Calculation	New Calculation
Electricity	Wet Electrostatic Precipitator	✓	✓
	Induced Draft Fan	✓	✓
	Wastewater Treatment Unit	✓	✓
	Continuous Emissions Monitoring System		✓
	Drum Storage Warehouse	✓	✓
	Carbon Product Storage Warehouse	✓	✓
	Administrative Offices	✓	✓
Natural Gas	Fans, Pumps, Motors		✓
	Burners in Furnace	✓	✓
	Small Boiler	✓	✓
	Burners in Afterburner	✓	✓
Water	Carbon Regeneration System	✓	✓
	Other Industrial Site Uses	✓	✓
	Administrative Offices	✓	✓
Other	Transportation		✓
	Laboratory analyses		✓
	Treatment chemicals		✓

Limitations

My study focused on one facility in Arizona; consequently, the generalizability of my results may be limited. Though the setup of each thermal reactivation facility is generally the same (EPA 2000), differences in location can affect transportation patterns (Neff 2005), electricity sources, and electricity and natural gas usage (Druckman 2008, Ratti 2005). These variations must be accounted for in a general environmental impact assessment of GAC regeneration.

The accuracy of my results was also impacted by the availability of context-dependent conversion factors for the calculations. Many conversion factors (e.g. energy consumption of an office building) were taken from national averages and tailored with rough estimates and assumptions (e.g. the on-site WWTP consumes half the average electricity of a typical WWTP). The accuracy of these assumptions has the potential to significantly affect the results.

Natural gas consumption, one of the largest contributors to the environmental footprint, is calculated directly from process drawings, which are assumed to be highly representative of the facility's resource flows (Scheuermann, personal communication). Thus, I am confident that variability in other impact categories (electricity and water) will have a small impact on the total carbon dioxide emissions with respect to the natural gas impact.

Future Directions

One improvement to my study would be to expand my system boundaries to include more environmental impact categories. Environmental impacts omitted from my analysis include hazardous waste generation and land use change impacts of regeneration activities.

Another improvement would be to investigate assumptions used in my calculations. For example, I assumed the on-site WWTP required half the electricity usage of a standard WWTP. In reality, the electricity consumption of the WWTP could be substantially higher or lower, depending on the treatment required (information on on-site wastewater treatment was not publicly available). I could also install water consumption, electricity consumption, and natural gas consumption meters at facility to determine the actual facility, warehouse, and office

resource consumption. Installing meters would also provide the opportunity to quantify the impact of activities that are not detailed in the permit application.

A comprehensive impact assessment of carbon regeneration requires analyzing a diversity of carbon regeneration facilities. An aggregate, precise impact assessment is impossible without analysis of multiple, differentially located thermal GAC regeneration facilities. Having a diverse portfolio of regeneration types (including thermal regeneration) will help remedial project managers to make more informed, actionable decisions about remediation design. Regeneration environmental impacts must also be compared to the impacts of used GAC disposal. A recalculation of the environmental impact will be necessary as regeneration practices change with improving technologies.

Broader Implications/ Conclusions

There are substantial environmental impacts associated with regenerating GAC. Prominent sources of carbon dioxide emissions were the electricity usage associated with the ID fan and the natural gas usage associated with burner operation. However, these environmental impacts are substantially less than those of generating virgin GAC. Overall, generating new GAC releases over eight times as much carbon dioxide equivalents as generating new GAC (Table 1). This conclusion should encourage remedial project managers to use regenerated GAC in their remediation projects.

By including more accurate and thorough impact calculations, decision-makers can more effectively apply green remediation principles to their projects. Comprehensive environmental footprint calculations also identify opportunities to modify processes to reduce environmental impacts and suggest which specific aspects of these processes have the highest potential for improvement. My study advances the ongoing process to improve EPA remediation projects through modifying remediation processes and presenting more environmentally sustainable remediation alternatives.

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REFERENCES

American Physical Society (APS). 2012. Energy Units. Accessed May 2012. [http://www.aps.org/policy/reports/popa-reports/energy/units.cfm]

Arizona Power Supply (APS). 2009. Arizona's Energy Future – APS Resource Plan 2009 Through 2025. Accessed May 2012. [http://www.aps.com/_files/various/ResourceAlt/Resource_Plan_-_Presentation_sFinal.pdf]

Bayer, P., H. Edda, U. Karl, and M. Finkel. 2005. Economical and ecological comparison of granular activated carbon (GAC) adsorber refill strategies. Water Research **39**:1719-1728.

California Department of Water Resources (CA DWR). 1994. Water Efficiency Guide for Business Managers and Facility Engineers. Accessed May 2012. [http://www.water.ca.gov/wateruseefficiency/docs/water_efficiency_guide.pdf]

Cannon, F. S., V. L. Snoeyink, R. G. Lee, and G. Dagois. 1994. Reaction mechanism of calcium catalyzed thermal regeneration of spent granular activated carbon. Carbon 32:1285-1301.

Clean Gas Systems, Inc. 2010. Wet Electrostatic Precipitators. Accessed December 2011. [http://www.cgscgs.com/pdf/pg12.pdf]

Consortium for Energy Efficiency (CEE). 2009. Factsheet: Motors and Motor Systems. Accessed April 2012. [http://www.cee1.org/resrc/facts/facts-main.php3]

Deru, M. 2007. Establishing Standard Source Energy and Emission Factors for Energy Use in Buildings. ASME Conference Proceedings 2007:541–548. doi: 10.1115/ES2007-36105.

Druckman, A., and T. Jackson. 2008. Household energy consumption in the UK: A highly geographically and socio-economically disaggregated model. Energy Policy 36:3177–3192. doi: 10.1016/j.enpol.2008.03.021.

E Source Companies LLC. 2006. Commercial Energy Advisor. Accessed December 2011. [http://www.esource.com/BEA/demo/PDF/CEA_offices.pdf]

E Source Companies LLC. 2007. Improving Energy Efficiency in Warehouses. Accessed March 2012. [http://www.touchstoneenergy.com/efficiency/bea/Documents/Warehouses.pdf]

Emissions & Generation Resource Integrated Database (eGRID). 2007. Year 2007 Summary Tables. Accessed March 2012. [http://www.epa.gov/cleanenergy/energy-resources/egrid/]

Energy Information Administration. 2011. Electric Sales, Revenue, and Average Price – Table T2: Sales to be Bundled and Unbundled Consumers by Sector, Census Division, and State, 2010. Accessed April 2012. [http://www.eia.gov/electricity/sales_revenue_price/pdf/table2.pdf]

Energy Information Administration. 2012. SEDS: State Energy Data System – Natural Gas Consumption 2010. Accessed April 2012. [http://www.eia.gov/state/seds/seds-data-fuel.cfm#ng].

Environmental Protection Agency (EPA) Superfund. 2004. Record of Decision: Iron Mountain Mine, Redding, CA.

Environmental Protection Agency (EPA). 2000. Wastewater Technology Fact Sheet: Granular Activated Carbon Adsorption and Regeneration. Office of Water, Municipal Technology Branch.

Environmental Protection Agency (EPA). 2009a. Authorization to Discharge under the National Pollutant Discharge Elimination System: NPDES Permit No. AZ0021415. Accessed December 2011. [http://www.epa.gov/region9/water/npdes/pdf/az/CRSSJV-Final-Permit_7_24_09.pdf]

Environmental Protection Agency (EPA). 2009b. National Pollutant Discharge Elimination System Proposed Permit Fact Sheet. Accessed December 2011. [http://www.epa.gov/region9/water/npdes/pdf/az/CRSSJV-Final-Fact-Sheet.pdf].

Environmental Protection Agency (EPA). 2010. BP Wood River Footprint Analysis is: Life-Cycle Energy and Emissions for Municipal Water and Wastewater Services: Case-Studies of Treatment Plants in US, Appendix B. http://www.clu-in.org/greenremediation/bpwoodriver/. Accessed May 2012

Environmental Protection Agency (EPA). 2011a. EPA History | About EPA | US EPA. Environmental Protection Agency. <http://www.epa.gov/aboutepa/history/index.html>

Environmental Protection Agency (EPA). 2011b. Superfund | US EPA. Environmental Protection Agency. <http://www.epa.gov/superfund/>.

Environmental Protection Agency (EPA). 2012. Methodology for Understanding and Reducing a Project's Environmental Footprint. Accessed May 2012. [http://www.cluin.org/greenremediation/methodology/docs/GC_Footprint_Methodology_Feb2012.pdf]

Google. 2012. Google Maps. Accessed May 2012. [www.maps.google.com]

Mandi, R. P., and U. R. Yaragatti. 2008. Enhancing Energy Efficiency of Induced Draft Fans in Thermal Power Plants. ACTA Press. Retrieved March 25, 2012, from http://www.actapress.com/Abstract.aspx?paperId=33345.

McLean-Conner, P. 2009. Energy Efficiency – Principles and Practices. PennWell. Accessed April 2012. [http://www.knovel.com/web/portal/browse/display?_EXT_KNOVEL_DISPLAY_bookid=3825&VerticalID=0]

Mohan, D., and K. P. Singh. 2005. Granular Activated Carbon. doi: 10.1002/047147844X.mw166.

Neff, R. J. 2005. Transportation, Urban Development, and Greenhouse Gases: Patterns of consumption and justice in Philadelphia, Pennsylvania. Thesis. [ftp://www.ce.cmu.edu/GDRG/Public/www/readings/2007/03/27/Neff_TransportationUrbanDevelopmentAndGHGs_PatternsOfConsumptionAndJusticeInPhiladelphiaPA.pdf]

Ratti, C., N. Baker, and K. Steemers. 2005. Energy consumption and urban texture. Energy and Buildings 37:762–776. doi: 10.1016/j.enbuild.2004.10.010.

Region 9: Superfund. 2011. Site Overview|Iron Mountain Mine|US EPA|Region 9|Superfund. Environmental Protection Agency. <http://yosemite.epa.gov/r9/sfund/r9sfdocw.nsf/vwsoalphabetic/Iron+Mountain+Mine?OpenDocument>.

San Miguel, G., S. . Lambert, and N. J. . Graham. 2001. The regeneration of field-spent granular-activated carbons. Water Research 35:2740-2748. doi: 10.1016/S0043-1354(00)00549-2.

Scheuermann, K. 2011. Calculation of the Footprint of Granular Activated Carbon Regeneration.

Seneviratne, Mohan. 2007. A practical approach to water conservation for commercial and industrial facilities. Accessed December 2011. [http://books.google.com/books?id=6k_PFbfGAUIC&pg=PA270&lpg=PA270&dq=%22water+usage%22+office+space&source=bl&ots=MIAwqLtJvB&sig=KfeBLGzBofmc4JRMkE5eUH2qieE&hl=en&ei=aOcsTcKUBYKB8gaJtvTnCQ&sa=X&oi=book_result&ct=result&resnum=4&ved=0CCIQ6AEwAw#v=onepage&q=%22water%20usage%22%20office%20space&f=false]

Siemens Water Technologies, Corp. 2007. Carbon Reactivation Facility RCRA Part B Permit Application. Accessed December 2011. [http://www.epa.gov/region9/waste/siemens/permit.html]

Spirax Sarco. 2012. Steam Tables. Accessed May 2012. [http://www.spiraxsarco.com/resources/steam-tables.asp]

ABBREVIATIONS AND ACRONYMS

acfm	actual cubic feet per minute
bhp	brake horsepower
Btu	British thermal unit
CEMS	continuous emissions monitoring system
EPA	environmental protection agency
GAC	granular activated carbon
HAP	hazardous air pollutant
ID	induced draft
kWh	kilowatt hour
NO_x	oxides of nitrogen
PM_{10}	particulate matter with a diameter of 10 microns or less
POTW	publicly owned treatment works
scfm	standard cubic feet per minute
SO_x	oxides of sulfur
SVOC	semi-volatile organic compound
VA	volt-ampere
VOC	volatile organic compound
WESP	wet electrostatic precipitator
WWTP	wastewater treatment plant

Treatment Technology Review and Assessment

Association of Washington Business
Association of Washington Cities
Washington State Association of Counties

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Acronyms

Acronym	Definition
AACE	Association for the Advancement of Cost Engineering
AOP	advanced oxidation processes
AWB	Association of Washington Businesses
BAC	biological activated carbon
BAP	benzo(a)pyrene
BOD	biochemical oxygen demand
BTU	British thermal unit
CEPT	Chemically-enhanced primary treatment
cf	cubic feet
CIP	clean in place
CRITFC	Columbia River Inter-Tribal Fish Commission
Ecology	Washington Department of Ecology
EPA	U.S. Environmental Protection Agency
FCR	fish consumption rate
g/day	grams per day
GAC	granular activated carbon
gal	gallon
gfd	gallons per square foot per day
GHG	greenhouse gas
gpd	gallons per day
gpm	gallons per minute
GWh	giga watt hours
HDR	HDR Engineering, Inc.
HHWQC	human health water quality criteria
HRT	hydraulic residence time
IPCC	Intergovernmental Panel on Climate Change
kg	kilogram
KWh/MG	kilowatt-hours per million gallons
lb	pound
MBR	membrane bioreactor
MCL	maximum contaminant level
MF	microfiltration
mgd	million gallons per day
mg/L	milligrams per liter
MMBTU	million British thermal units
MWh/d	megawatt-hours per day
NF	nanofiltration
ng/L	nanograms per liter
NPDES	National Pollutant Discharge Elimination System
NPV	net present value
O&M	operations and maintenance
ODEQ	Oregon Department of Environmental Quality
PAC	powdered activated carbon
PAH	polycyclic aromatic hydrocarbons
PCB	polychlorinated biphenyls
PE	population equivalents
PIX	potable ion exchange

Acronym	Definition
ppm	parts per million
RO	reverse osmosis
SDWA	Safe Drinking Water Act
sf	square feet
SGSP	salinity gradient solar pond
SRT	solids retention time
Study Partners	Association of Washington Businesses/Association of Washington Cities and Washington State Association of Counties consortium
TDS	total dissolved solids
TMDL	total maximum daily load
TSS	total suspended solids
UF	ultrafiltration
µg/L	micrograms per liter
USDA	U.S. Department of Agriculture
UV	ultraviolet
WAC	Washington Administrative Code
WAS	waste activated sludge
WLA	waste load allocation
WWTP	wastewater treatment plant
ZLD	zero liquid discharge

Executive Summary

This study evaluated treatment technologies potentially capable of meeting the State of Washington Department of Ecology's (Ecology) revised effluent discharge limits associated with revised human health water quality criteria (HHWQC). HDR Engineering, Inc. (HDR) completed a literature review of potential technologies and an engineering review of their capabilities to evaluate and screen treatment methods for meeting revised effluent limits for four constituents of concern: arsenic, benzo(a)pyrene (BAP), mercury, and polychlorinated biphenyls (PCBs). HDR selected two alternatives to compare against an assumed existing baseline secondary treatment system utilized by dischargers. These two alternatives included enhanced secondary treatment with membrane filtration/reverse osmosis (MF/RO) and enhanced secondary treatment with membrane filtration/granulated activated carbon (MF/GAC). HDR developed capital costs, operating costs, and a net present value (NPV) for each alternative, including the incremental cost to implement improvements for an existing secondary treatment facility.

Currently, there are no known facilities that treat to the HHWQC and anticipated effluent limits that are under consideration. Based on the literary review, research, and bench studies, the following conclusions can be made from this study:

- Revised HHWQC based on state of Oregon HHWQC (2001) and U.S. Environmental Protection Agency (EPA) "National Recommended Water Quality Criteria" will result in very low water quality criteria for toxic constituents.
- There are limited "proven" technologies available for dischargers to meet required effluent quality limits that would be derived from revised HHWQC.
    - Current secondary wastewater treatment facilities provide high degrees of removal for toxic constituents; however, they are not capable of compliance with water quality-based National Pollutant Discharge Elimination System (NPDES) permit effluent limits derived from the revised HHWQC.
    - Advanced treatment technologies have been investigated and candidate process trains have been conceptualized for toxics removal.
        - Advanced wastewater treatment technologies may enhance toxics removal rates; however, they will not be capable of compliance with HHWQC-based effluent limits for PCBs. The lowest levels achieved based on the literature review were between <0.00001 and 0.00004 micrograms per liter (µg/L), as compared to a HHWQC of 0.0000064 µg/L.
        - Based on very limited performance data for arsenic and mercury from advanced treatment information available in the technical literature, compliance with revised criteria may or may not be possible, depending upon site specific circumstances.
            - Compliance with a HHWQC for arsenic of 0.018 µg/L appears unlikely. Most treatment technology performance information available in the literature is based on drinking water treatment applications targeting a much higher Safe Drinking Water Act (SDWA) maximum contaminant level (MCL) of 10 µg/L.
            - Compliance with a HHWQC for mercury of 0.005 µg/L appears to be potentially attainable on an average basis, but perhaps not if effluent limits are structured on a maximum monthly, maximum weekly or maximum daily basis. Some secondary treatment facilities attain average effluent mercury levels of 0.009 to 0.066 µg/L. Some treatment facilities with effluent filters attain average effluent mercury levels of 0.002 to 0.010 µg/L. Additional

advanced treatment processes are expected to enhance these removal rates, but little mercury performance data is available for a definitive assessment.

- Little information is available to assess the potential for advanced technologies to comply with revised BAP criteria. A municipal wastewater treatment plant study reported both influent and effluent BAP concentrations less than the HHWQC of 0.0013 ug/L (Ecology, 2010).

- Some technologies may be effective at treating identified constituents of concern to meet revised limits while others may not. It is therefore even more challenging to identify a technology that can meet all constituent limits simultaneously.
- A HHWQC that is one order-of-magnitude less stringent could likely be met for mercury and BAP; however, it appears PCB and arsenic limits would not be met.

- Advanced treatment processes incur significant capital and operating costs.
  - Advanced treatment process to remove additional arsenic, BAP, mercury, and PCBs would combine enhancements to secondary treatment with microfiltration membranes and reverse osmosis or granular activated carbon and increase the estimated capital cost of treatment from $17 to $29 in dollars per gallon per day of capacity (based on a 5.0-million-gallon-per-day (mgd) facility).
  - The annual operation and maintenance costs for the advanced treatment process train will be substantially higher (approximately $5 million - $15 million increase for a 5.0 mgd capacity facility) than the current secondary treatment level.
- Implementation of additional treatment will result in additional collateral impacts.
  - High energy consumption.
  - Increased greenhouse gas emissions.
  - Increase in solids production from chemical addition to the primaries. Additionally, the membrane and GAC facilities will capture more solids that require handling.
  - Increased physical space requirements at treatment plant sites for advanced treatment facilities and residuals management including reverse osmosis reject brine processing.
- It appears advanced treatment technology alone cannot meet all revised water quality limits and implementation tools are necessary for discharger compliance.
  - Implementation flexibility will be necessary to reconcile the difference between the capabilities of treatment processes and the potential for HHWQC driven water quality based effluent limits to be lower than attainable with technology

Table ES-1 indicates that the unit NPV cost for baseline conventional secondary treatment ranges from $13 to $28 per gallon per day of treatment capacity. The unit cost for the advanced treatment alternatives increases the range from the low $20s to upper $70s on a per gallon per-day of treatment capacity. The resulting unit cost for improving from secondary treatment to advanced treatment ranges between $15 and $50 per gallon per day of treatment capacity. Unit costs were also evaluated for both a 0.5 and 25 mgd facility. The range of unit costs for improving a 0.5 mgd from secondary to advanced treatment is $60 to $162 per gallon per day of treatment capacity. The range of unit costs for improving a 25 mgd from secondary to advanced treatment is $10 to $35 per gallon per day of treatment capacity.

Table ES-1. Treatment Technology Costs in 2013 Dollars for a 5-mgd Facility

Alternative	Total Construction Cost, 2013 dollars ($ Million)	O&M Net Present Value, 2013 dollars ($ Million)***	Total Net Present Value, 2013 dollars ($ Million)	NPV Unit Cost, 2013 dollars ($/gpd)
Baseline (Conventional Secondary Treatment)*	59 - 127	5 - 11	65 - 138	13 - 28
Incremental Increase to Advanced Treatment - MF/RO	48 - 104	26 - 56	75 - 160	15 - 32
Advanced Treatment - MF/RO**	108 - 231	31 - 67	139 - 298	28 - 60
Incremental Increase to Advanced Treatment - MF/GAC	71 - 153	45 - 97	117 - 250	23 - 50
Advanced Treatment - MF/GAC	131 - 280	50 - 108	181 - 388	36 - 78

* Assumed existing treatment for dischargers. The additional cost to increase the SRT to upwards of 30-days is about $12 - 20 million additional dollars in total project cost for a 5 mgd design flow.

** Assumes zero liquid discharge for RO brine management, followed by evaporation ponds. Other options are available as listed in Section 4.4.2.

*** Does not include the cost for labor.

mgd=million gallons per day
MG=million gallons
MF/RO=membrane filtration/reverse osmosis
MF/GAC=membrane filtration/granulated activated carbon
O&M=operations and maintenance
Net Present Value = total financed cost assuming a 5% nominal discount rate over an assumed 25 year equipment life.

Costs presented above are based on a treatment capacity of 5.0 mgd, however, existing treatment facilities range dramatically across Washington in size and flow treated. The key differences in cost between the baseline and the advanced treatment MF/RO are as follows:

- Larger aeration basins than the baseline to account for the longer SRT (>8 days versus <8 days).
- Additional pumping stations to pass water through the membrane facilities and granulated activated carbon facilities. These are based on peak flows.
- Membrane facilities (equipment, tanks chemical feed facilities, pumping, etc.) and replacement membrane equipment.
- Granulated activated carbon facilities (equipment, contact tanks, pumping, granulated activated carbon media, etc.)
- Additional energy and chemical demand to operate the membrane and granulated activated carbon facilities
- Additional energy to feed and backwash the granulated activated carbon facilities.
- Zero liquid discharge facilities to further concentrate the brine reject.
    - Zero liquid discharge facilities are energy/chemically intensive and they require membrane replacement every few years due to the brine reject water quality.
- Membrane and granulated activated carbon media replacement represent a significant maintenance cost.

- Additional hauling and fees to regenerate granulated activated carbon off-site.

The mass of pollutant removal by implementing advanced treatment was calculated based on reducing current secondary effluent discharges to revised effluent limits for the four pollutants of concern. These results are provided in Table ES-2 as well as a median estimated unit cost basis for the mass of pollutants removed.

Table ES-2. Unit Cost by Contaminant for a 5-mgd Facility Implementing Advanced Treatment using Membrane Filtration/Reverse Osmosis

Component	PCBs	Mercury	Arsenic	BAPs
Required HHWQC based Effluent Quality (µg/L)	0.0000064	0.005	0.018	0.0013
Current Secondary Effluent Concentration (µg/L)	0.002	0.025	7.5	0.006
Total Mass Removed (lbs) over 25 year Period	0.76	7.6	2,800	1.8
Median Estimated Unit Cost (NPV per total mass removed in pounds over 25 years)	$290,000,000	$29,000,000	$77,000	$120,000,000

µg/L=micrograms per liter
lbs=pounds
NPV=net present value

Collateral adverse environmental impacts associated with implementing advanced treatment were evaluated. The key impacts from this evaluation include increased energy use, greenhouse gas production, land requirements and treatment residuals disposal. Operation of advanced treatment technologies could increase electrical energy by a factor of 2.3 to 4.1 over the baseline secondary treatment system. Direct and indirect greenhouse gas emission increases are related to the operation of advanced treatment technologies and electrical power sourcing, with increases of at least 50 to 100 percent above the baseline technology. The energy and air emission implications of advanced treatment employing granulated activated carbon construction of advanced treatment facilities will require additional land area. The availability and cost of land adjacent to existing treatment facilities has not been included in cost estimates, but could be very substantial. It is worthwhile noting residual materials from treatment may potentially be hazardous and their disposal may be challenging to permit. Costs assume zero liquid discharge from the facilities.

1.0 Introduction

Washington's Department of Ecology (Ecology) has an obligation to periodically review waterbody "designated uses" and to modify, as appropriate, water quality standards to ensure those uses are protected. Ecology initiated this regulatory process in 2009 for the human health-based water quality criteria (HHWQC) in Washington's *Surface Water Quality Standards* (Washington Administrative Code [WAC] 173-201A). HHWQC are also commonly referred to as "toxic pollutant water quality standards." Numerous factors will influence Ecology's development of HHWQC. The expectation is that the adopted HHWQC will be more stringent than current adopted criteria. National Pollutant Discharge Elimination System (NPDES) effluent limits for permitted dischargers to surface waters are based on U.S. Environmental Protection Agency (EPA) and state guidance. Effluent limits are determined primarily from reasonable potential analyses and waste load allocations (WLAs) from total maximum daily loads (TMDLs), although the permit writer may use other water quality data. Water quality-based effluent limits are set to be protective of factors, including human health, aquatic uses, and recreational uses. Therefore, HHWQC can serve as a basis for effluent limits. The presumption is that more stringent HHWQC will, in time, drive lower effluent limits. The lower effluent limits will require advanced treatment technologies and will have a consequent financial impact on NPDES permittees. Ecology anticipates that a proposed revision to the water quality standards regulation will be issued in first quarter 2014, with adoption in late 2014.

The Association of Washington Businesses (AWB) is recognized as the state's chamber of commerce, manufacturing and technology association. AWB members, along with the Association of Washington Cities and Washington State Association of Counties (collectively referred to as Study Partners), hold NPDES permits authorizing wastewater discharges. The prospect of more stringent HHWQC, and the resulting needs for advanced treatment technologies to achieve lower effluent discharge limits, has led this consortium to sponsor a study to assess technology availability and capability, capital and operations and maintenance (O&M) costs, pollutant removal effectiveness, and collateral environmental impacts of candidate technologies.

The "base case" for the study began with the identification of four nearly ubiquitous toxic pollutants present in many industrial and municipal wastewater discharges, and the specification of pollutant concentrations in well-treated secondary effluent. The pollutants are arsenic, benzo(a)pyrene (BAP), mercury and polychlorinated biphenyls (PCBs), which were selected for review based on available monitoring data and abundant presence in the environment. The purpose of this study is to review the potential water quality standards and associated treatment technologies able to meet those standards for four pollutants.

A general wastewater treatment process and wastewater characteristics were used as the common baseline for comparison with all of the potential future treatment technologies considered. An existing secondary treatment process with disinfection at a flow of 5 million gallons per day (mgd) was used to represent existing conditions. Typical effluent biochemical oxygen demand (BOD) and total suspended solids (TSS) were assumed between 10 and 30 milligrams per liter (mg/L) for such a facility and no designed nutrient or toxics removal was assumed for the baseline existing treatment process.

Following a literature review of technologies, two advanced treatment process options for toxics removal were selected for further evaluation based on the characterization of removal effectiveness from the technical literature review and Study Partners' preferences. The two tertiary treatment options are microfiltration membrane filtration (MF) followed by either reverse osmosis (RO) or granular activated carbon (GAC) as an addition to an existing secondary treatment facility.

The advanced treatment technologies are evaluated for their efficacy and cost to achieve the effluent limitations implied by the more stringent HHWQC. Various sensitivities are examined, including for less stringent adopted HHWQC, and for a size range of treatment systems. Collateral environmental impacts associated with the operation of advanced technologies are also qualitatively described.

2.0 Derivation of the Baseline Study Conditions and Rationale for Selection of Effluent Limitations

2.1 Summary of Water Quality Criteria

Surface water quality standards for toxics in the State of Washington are being updated based on revised human fish consumption rates (FCRs). The revised water quality standards could drive very low effluent limitations for industrial and municipal wastewater dischargers. Four pollutants were selected for study based on available monitoring data and abundant presence in the environment. The four toxic constituents are arsenic, BAP, mercury, and PCBs.

2.2 Background

Ecology is in the process of updating the HHWQC in the state water quality standards regulation. Toxics include metals, pesticides, and organic compounds. The human health criteria for toxics are intended to protect people who consume water, fish, and shellfish. FCRs are an important factor in the derivation of water quality criteria for toxics.

The AWB/City/County consortium (hereafter "Study Partners") has selected four pollutants for which more stringent HHWQC are expected to be promulgated. The Study Partners recognize that Ecology probably will not adopt more stringent arsenic HHWQC so the evaluation here is based on the current arsenic HHWQC imposed by the National Toxics Rule. Available monitoring information indicates these pollutants are ubiquitous in the environment and are expected to be present in many NPDES discharges. The four pollutants include the following:

- Arsenic
  - Elemental metalloid that occurs naturally and enters the environment through erosion processes. Also widely used in batteries, pesticides, wood preservatives, and semiconductors. Other current uses and legacy sources in fungicides/herbicides, copper smelting, paints/dyes, and personal care products.

- Benzo(a)pyrene (BAP)
  - Benzo(a)pyrene is a polycyclic aromatic hydrocarbon formed by a benzene ring fused to pyrene as the result of incomplete combustion. Its metabolites are highly carcinogenic. Sources include wood burning, coal tar, automobile exhaust, cigarette smoke, and char-broiled food.

- Mercury
  - Naturally occurring element with wide legacy uses in thermometers, electrical switches, fluorescent lamps, and dental amalgam. Also enters the environment through erosion processes, combustion (especially coal), and legacy industrial/commercial uses. Methylmercury is an organometallic that is a bioaccumulative toxic. In aquatic systems, an anaerobic methylation process converts inorganic mercury to methylmercury.

- Polychlorinated Biphenyls (PCBs)
  - Persistent organic compounds historically used as a dielectric and coolant in electrical equipment and banned from production in the U.S. in 1979. Available information indicates continued pollutant loadings to the environment as a byproduct from the use of some pigments, paints, caulking, motor oil, and coal combustion.

2.3 Assumptions Supporting Selected Ambient Water Quality Criteria and Effluent Limitations

Clean Water Act regulations require NPDES permittees to demonstrate their discharge will "not cause or contribute to a violation of water quality criteria." If a "reasonable potential analysis" reveals the possibility of a standards violation, the permitting authority is obliged to develop "water quality-based effluent limits" to ensure standards achievement. In addition, if ambient water quality monitoring or fish tissue assessments reveal toxic pollutant concentrations above HHWQC levels, Ecology is required to identify that impairment ("303(d) listing") and develop corrective action plans to force reduction in the toxic pollutant discharge or loading of the pollutant into the impaired water body segment. These plans, referred to as total maximum daily loads (TMDLs) or water cleanup plans, establish discharge allocations and are implemented for point discharge sources through NPDES permit effluent limits and other conditions.

The effect of more stringent HHWQC will intuitively result in more NPDES permittees "causing or contributing" to a water quality standards exceedance, and/or more waterbodies being determined to be impaired, thus requiring 303(d) listing, the development of TMDL/water cleanup plans, and more stringent effluent limitations to NPDES permittees whose treated wastewater contains the listed toxic pollutant.

The study design necessarily required certain assumptions to create a "baseline effluent scenario" against which the evaluation of advanced treatment technologies could occur. The Study Partners and HDR Engineering, Inc (HDR) developed the scenario. Details of the baseline effluent scenario are presented in Table 1. The essential assumptions and rationale for selection are presented below:

- Ecology has indicated proposed HHWQC revisions will be provided in first quarter 2014. A Study Partners objective was to gain an early view on the treatment technology and cost implications. Ecology typically allows 30 or 45 days for the submission of public comments on proposed regulations. To wait for the proposed HHWQC revisions would not allow sufficient time to complete a timely technology/cost evaluation and then to share the study results in the timeframe allowed for public involvement/public comments.
- Coincident with the issuance of the proposed regulation, Ecology has a statutory obligation to provide a Significant Legislative Rule evaluation, one element of which is a "determination whether the probable benefits of the rule are greater than its probable costs, taking into account both the qualitative and quantitative benefits and costs and the specific directives of the statute being implemented" (RCW 34.05.328(1)(d)). A statutory requirement also exists to assess the impact of the proposed regulation to small businesses. The implication is that Ecology will be conducting these economic evaluations in fourth quarter 2013 and early 2014. The Study Partners wanted to have a completed technology/cost study available to share with Ecology for their significant legislative rule/small business evaluations.
- The EPA, Indian tribes located in Washington, and various special interest groups have promoted the recently promulgated state of Oregon HHWQC (2011) as the "model" for Washington's revisions of HHWQC. The Oregon HHWQC are generally based on a increased FCR of 175 grams per day (g/day) and an excess cancer risk of 10^{-6}. While the Study Partners do not concede the wisdom or appropriateness of the Oregon criteria, or the selection of scientific/technical elements used to derive those criteria, the Study Partners nevertheless have selected the Oregon HHWQC as a viable "starting point" upon which this study could be based.

- The scenario assumes generally that Oregon's HHWQC for ambient waters will, for some parameters in fact, become effluent limitations for Washington NPDES permittees. The reasoning for this important assumption includes:
    - The state of Washington's NPDES permitting program is bound by the *Friends of Pinto Creek vs. EPA* decision in the United States Court of Appeals for the Ninth Circuit (October 4, 2007). This decision held that no NPDES permits authorizing new or expanded discharges of a pollutant into a waterbody identified as impaired; i.e., listed on CWA section 303(d), for that pollutant, may be issued until such time as "existing dischargers" into the waterbody are "subject to compliance schedules designed to bring the (waterbody) into compliance with applicable water quality standards." In essence, any new/expanded discharge of a pollutant causing impairment must achieve the HHWQC at the point of discharge into the waterbody.
    - If a waterbody segment is identified as "impaired" (i.e., not achieving a HHWQC), then Ecology will eventually need to produce a TMDL or water cleanup plan. For an existing NPDES permittee with a discharge of the pollutant for which the receiving water is impaired, the logical assumption is that any waste load allocation granted to the discharger will be at or lower than the numeric HHWQC (to facilitate recovery of the waterbody to HHWQC attainment). As a practical matter, this equates to an effluent limit established at the HHWQC.
    - Acceptance of Oregon HHWQC as the baseline for technology/cost review also means acceptance of practical implementation tools used by Oregon. The HHWQC for mercury is presented as a fish tissue methyl mercury concentration. For the purposes of NPDES permitting, however, Oregon has developed an implementation management directive which states that any confirmed detection of mercury is considered to represent a "reasonable potential" to cause or contribute to a water quality standards violation of the methyl mercury criteria. The minimum quantification level for total mercury is presented as 0.005 micrograms per liter (µg/L) (5.0 nanograms per liter (ng/L)).
    - The assumed effluent limit for arsenic is taken from EPA's *National Recommended Water Quality Criteria* (2012) (inorganic, water and organisms, 10^{-6} excess cancer risk). Oregon's 2011 criterion is actually based on a less protective excess cancer risk (10^{-4}). This, however, is the result of a state-specific risk management choice and it is unclear if Washington's Department of Ecology would mimic the Oregon approach.
    - The assumption is that no mixing zone is granted such that HHWQC will effectively serve as NPDES permit effluent limits. Prior discussion on the impact of the Pinto Creek decision, 303(d) impairment and TMDL Waste Load Allocations processes, all lend support to this "no mixing zone" condition for the parameters evaluated in this study.
- Consistent with Ecology practice in the evaluation of proposed regulations, the HHWQC are assumed to be in effect for a 20-year period. It is assumed that analytical measurement technology and capability will continue to improve over this time frame and this will result in the detection and lower quantification of additional HHWQC in ambient water and NPDES dischargers. This knowledge will trigger the Pinto Creek/303(d)/TMDL issues identified above and tend to pressure NPDES permittees to evaluate and install advanced treatment technologies. The costs and efficacy of treatment for these additional HHWQC is unknown at this time.

Other elements of the Study Partners work scope, as presented to HDR, must be noted:

- The selection of four toxic pollutants and development of a baseline effluent scenario is not meant to imply that each NPDES permittee wastewater discharge will include those pollutants at the assumed concentrations. Rather, the scenario was intended to represent a composite of many NPDES permittees and to facilitate evaluation of advanced treatment technologies relying on mechanical, biological, physical, chemical processes.
- The scalability of advanced treatment technologies to wastewater treatment systems with different flow capacities, and the resulting unit costs for capital and O&M, is evaluated.
- Similarly, a sensitivity analysis on the unit costs for capital and O&M was evaluated on the assumption the adopted HHWQC (and effectively, NPDES effluent limits) are one order-of-magnitude less stringent than the Table 1 values.

Table 1: Summary of Effluent Discharge Toxics Limits

Constituent	Human Health Criteria based Limits to be met with no Mixing Zone (µg/L)	Basis for Criteria	Typical Concentration in Municipal Secondary Effluent (µg/L)	Typical Concentration in Industrial Secondary Effluent (µg/L)	Existing Washington HHC (water + org.), NTR (µg/L)
PCBs	0.0000064	Oregon Table 40 Criterion (water + organisms) at FCR of 175 grams/day	0.0005 to 0.0025[b,c,d,e,f]	0.002 to 0.005[i]	0.0017
Mercury	0.005	DEQ IMD[a]	0.003 to 0.050[h]	0.010 to 0.050[h]	0.140
Arsenic	0.018	EPA National Toxics Rule (water + organisms)[k]	0.500 to 5.0[j]	10 to 40[j]	0.018
Benzo(a)Pyrene	0.0013	Oregon Table 40 Criterion (water + organisms) at FCR of 175 grams/day	0.00028 to 0.006[b,g]	0.006 to1.9	0.0028

[a] Oregon Department of Environmental Quality (ODEQ). Internal Management Directive: Implementation of Methylmercury Criterion in NPDES Permits. January 8, 2013.
[b] Control of Toxic Chemicals in Puget Sound, Summary Technical Report for Phase 3: Loadings from POTW Discharge of Treated Wastewater, Washington Department of Ecology, Publication Number 10-10-057, December 2010.
[c] Spokane River PCB Source Assessment 2003-2007, Washington Department of Ecology, Publication No. 11-03-013, April 2011.
[d] Lower Okanogan River Basin DDT and PCBs Total Maximum Daily Load, Submittal Report, Washington Department of Ecology, Publication Number 04-10-043, October 2004.
[e] Palouse River Watershed PCB and Dieldrin Monitoring, 2007-2008, Wastewater Treatment Plants and Abandoned Landfills, Washington Department of Ecology, Publication No. 09-03-004, January 2009
[f] A Total Maximum Daily Load Evaluation for Chlorinated Pesticides and PCBs in the Walla Walla River, Washington Department of Ecology, Publication No. 04-03-032, October 2004.
[g] Removal of Polycyclic Aromatic Hydrocarbons and Heterocyclic Nitrogenous Compounds by A POTW Receiving Industrial Discharges, Melcer, H., Steel, P. and Bedford, W.K., Water Environment Federation, 66th Annual Conference and Exposition, October 1993.
[h] Data provided by Lincoln Loehr's summary of WDOE Puget Sound Loading data in emails from July 19, 2013.
[i] NCASI memo from Larry Lefleur, NCASI, to Llewellyn Matthews, NWPPA, revised June 17, 2011, summarizing available PCB monitoring data results from various sources.
[j] Professional judgment, discussed in August 6, 2013 team call.
[k] The applicable Washington Human Health Criteria cross-reference the EPA National Toxics Rule, 40 CFR 131.36. The EPA arsenic HHC is 0.018 ug/L for water and organisms.

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3.0 Wastewater Characterization Description

This section describes the wastewater treatment discharge considered in this technology evaluation. Treated wastewater characteristics are described, including average and peak flow, effluent concentrations, and toxic compounds of concern.

3.1 Summary of Wastewater Characterization

A general wastewater treatment process and wastewater characteristics were developed as the common baseline to represent the existing conditions as a starting point for comparison with potential future advanced treatment technologies and improvements. A secondary treatment process with disinfection at a flow of 5 mgd as the current, baseline treatment system for existing dischargers was also developed. Typical effluent biochemical oxygen demand (BOD) and total suspended solids (TSS) were assumed between 10 to 30 mg/L from such a facility and no nutrient or toxics removal was assumed to be accomplished in the existing baseline treatment process.

3.2 Existing Wastewater Treatment Facility

The first step in the process is to characterize the existing wastewater treatment plant to be evaluated in this study. The goal is to identify the necessary technology that would need to be added to an existing treatment facility to comply with revised toxic pollutant effluent limits. Rather than evaluating the technologies and costs to upgrade multiple actual operating facilities, the Study Partners specified that a generalized municipal/industrial wastewater treatment facility would be characterized and used as the basis for developing toxic removal approaches. General characteristics of the facility's discharge are described in Table 2.

Table 2. General Wastewater Treatment Facility Characteristics

Average Annual Wastewater Flow, mgd	Maximum Month Wastewater Flow, mgd	Peak Hourly Wastewater Flow, mgd	Effluent BOD, mg/L	Effluent TSS, mg/L
5.0	6.25	15.0	10 to 30	10 to 30

mgd=million gallons per day
mg/L=milligrams per liter
BOD=biochemical oxygen demand
TSS=total suspended solids

In the development of the advanced treatment technologies presented below, the capacity of major treatment elements are generally sized to accommodate the maximum month average wastewater flow. Hydraulic elements, such as pumps and pipelines, were selected to accommodate the peak hourly wastewater flow.

The general treatment facility incorporates a baseline treatment processes including influent screening, grit removal, primary sedimentation, suspended growth biological treatment (activated sludge), secondary clarification, and disinfection using chlorine. Solids removed during primary treatment and secondary clarification are assumed to be thickened, stabilized, dewatered, and land applied to agricultural land. The biological treatment process is assumed to be activated sludge with a relatively short (less than 10-day) solids retention time. The baseline secondary treatment facility is assumed not to have processes dedicated to removing nutrients or toxics. However, some coincident removal of toxics will occur during conventional treatment.

3.3 Toxic Constituents

As described in Section 2.3, the expectation of more stringent HHWQC will eventually trigger regulatory demands for NPDES permittees to install advanced treatment technologies. The Study Group and HDR selected four specific toxic pollutants reflecting a range of toxic constituents as the basis for this study to limit the constituents and technologies to be evaluated to a manageable level.

The four toxic pollutants selected were PCBs, mercury, arsenic, and BAP, a polycyclic aromatic hydrocarbon (PAH). Mercury and arsenic are metals, and PCBs and PAHs are organic compounds. Technologies for removing metals and organic compounds are in some cases different. Key information on each of the compounds, including a description of the constituent, the significance of each constituent, proposed HHWQC, basis for the proposed criteria, typical concentration in both municipal and industrial secondary effluent, and current Washington state water quality criteria, are shown in Table 1. It is assumed that compliance with the proposed criteria in the table would need to be achieved at the “end of pipe” and Ecology would not permit a mixing zone for toxic constituents. This represents a “worst–case,” but a plausible assumption about discharge conditions.

4.0 Treatment Approaches and Costs

4.1 Summary of Treatment Approach and Costs

Two advanced treatment process options for toxics removal for further evaluation based on the characterization of removal effectiveness from the technical literature review and Study Group preferences. The two tertiary treatment options are microfiltration MF followed by either RO or GAC as an addition to an existing secondary treatment facility. Based on the literature review, it is not anticipated that any of the treatment options will be effective in reducing all of the selected pollutants to below the anticipated water quality criteria. A summary of the capital and operations and maintenance costs for tertiary treatment is provided, as well as a comparison of the adverse environmental impacts for each alternative.

4.2 Constituent Removal – Literature Review

The evaluation of treatment technologies relevant to the constituents of concern was initiated with a literature review. The literature review included a desktop search using typical web-based search engines, and search engines dedicated to technical and research journal databases. At the same time, HDR's experience with the performance of existing treatment technologies specifically related to the four constituents of concern, was used in evaluating candidate technologies. A summary of the constituents of concern and relevant treatment technologies is provided in the following literature review section.

4.2.1 Polychlorinated Biphenyls

PCBs are persistent organic pollutants that can be difficult to remove in treatment. PCB treatment in wastewater can be achieved using oxidation with peroxide, filtration, biological treatment or a combination of these technologies. There is limited information available about achieving ultra-low effluent PCB concentrations near the 0.0000064 µg/L range under consideration in the proposed rulemaking process. This review provides a summary of treatment technology options and anticipated effluent PCB concentrations.

Research on the effectiveness of ultraviolet (UV) light and peroxide on removing PCBs was tested in bench scale batch reactions (Yu, Macawile, Abella, & Gallardo 2011). The combination of UV and peroxide treatment achieved PCB removal greater than 89 percent, and in several cases exceeding 98 percent removal. The influent PCB concentration for the batch tests ranged from 50 to 100 micrograms per liter (µg/L). The final PCB concentration (for the one congener tested) was <10 µg/L (10,000 ng/L) for all tests and <5 µg/L (5,000 ng/L) for some tests. The lowest PCB concentrations in the effluent occurred at higher UV and peroxide doses.

Pilot testing was performed to determine the effectiveness of conventional activated sludge and a membrane bioreactor to remove PCBs (Bolzonella, Fatone, Pavan, & Cecchi 2010). EPA Method 1668 was used for the PCB analysis (detection limit of 0.01 ng/L per congener). Influent to the pilot system was a combination of municipal and industrial effluent. The detailed analysis was for several individual congeners. Limited testing using the Aroclor method (total PCBs) was used to compare the individual congeners and the total concentration of PCBs. Both conventional activated sludge and membrane bioreactor (MBR) systems removed PCBs. The effluent MBR concentrations ranged from <0.01 ng/L to 0.04 ng/L compared to <0.01 ng/L to 0.88 ng/L for conventional activated sludge. The pilot testing showed that increased solids retention time (SRT) and higher mixed liquor suspended solids concentrations in the MBR system led to increased removal in the liquid stream.

Bench scale studies were completed to test the effectiveness of GAC and biological activated carbon (BAC) for removing PCBs (Ghosh, Weber, Jensen, & Smith 1999). The effluent from the

GAC system was 800 ng/L. The biological film in the BAC system was presumed to support higher PCB removal with effluent concentrations of 200 ng/L. High suspended sediment in the GAC influent can affect performance. It is recommended that filtration be installed upstream of a GAC system to reduce solids and improve effectiveness.

Based on limited available data, it appears that existing municipal secondary treatment facilities in Washington state are able to reduce effluent PCBs to the range approximately 0.10 to 1.5 ng/L. It appears that the best performing existing municipal treatment facility in Washington state with a microfiltration membrane is able to reduce effluent PCBs to the range approximately 0.00019 to 0.00063 µg/L. This is based on a very limited data set and laboratory blanks covered a range that overlapped with the effluent results (blanks 0.000058 to 0.00061 µg/L).

Addition of advanced treatment processes would be expected to enhance PCB removal rates, but the technical literature does not appear to provide definitive information for guidance. A range of expected enhanced removal rates might be assumed to vary widely from level of the reference microfiltration facility of 0.19 to 0.63 ng/L.

Summary of PCB Technologies

The literature review revealed there are viable technologies available to reduce PCBs **but no research was identified with treatment technologies capable of meeting the anticipated human health criteria based limits for PCB removal**. Based on this review, a tertiary process was selected to biologically reduce PCBs and separate the solids using tertiary filtration. Alternately, GAC was investigated as an option to reduce PCBs, although it is not proven that it will meet revised effluent limits.

4.2.2 Mercury

Mercury removal from wastewater can be achieved using precipitation, adsorption, filtration, or a combination of these technologies. There is limited information available about achieving ultra-low effluent mercury concentrations near the 5 ng/L range under consideration in the proposed rulemaking process. This review provides a summary of treatment technology options and anticipated effluent mercury concentrations.

Precipitation (and co-precipitation) involves chemical addition to form a particulate and solids separation, using sedimentation or filtration. Precipitation includes the addition of a chemical precipitant and pH adjustment to optimize the precipitation reaction. Chemicals can include metal salts (ferric chloride, ferric sulfate, ferric hydroxide, or alum), pH adjustment, lime softening, or sulfide. A common precipitant for mercury removal is sulfide, with an optimal pH between 7 and 9. The dissolved mercury is precipitated with the sulfide to form an insoluble mercury sulfide that can be removed through clarification or filtration. One disadvantage of precipitation is the generation of a mercury-laden sludge that will require dewatering and disposal. The mercury sludge may be considered a hazardous waste and require additional treatment and disposal at a hazardous waste site. The presence of other compounds, such as other metals, may reduce the effectiveness of mercury precipitation/co-precipitation. For low-level mercury treatment requirements, several treatment steps will likely be required in pursuit of very low effluent targets.

EPA compiled a summary of facilities that are using precipitation/co-precipitation for mercury treatment (EPA 2007). Three of the full-scale facilities were pumping and treating groundwater and the remaining eight facilities were full-scale wastewater treatment plants. One of the pump and treat systems used precipitation, carbon adsorption, and pH adjustment to treat groundwater to effluent concentrations of 300 ng/L.

Adsorption treatment can be used to remove inorganic mercury from water. While adsorption can be used as a primary treatment step, it is frequently used for polishing after a preliminary treatment step (EPA 2007). One disadvantage of adsorption treatment is that when the adsorbent is saturated, it either needs to be regenerated or disposed of and replaced with new adsorbent. A common adsorbent is GAC. There are several patented and proprietary adsorbents on the market for mercury removal. Adsorption effectiveness can be affected by water quality characteristics, including high solids and bacterial growth, which can cause media blinding. A constant and low flow rate to the adsorption beds increases effectiveness (EPA 2007). The optimal pH for mercury adsorption on GAC is pH 4 to 5; therefore, pH adjustment may be required.

EPA compiled a summary of facilities that are using adsorption for mercury treatment (EPA 2007). Some of the facilities use precipitation and adsorption as described above. The six summarized facilities included two groundwater treatment and four wastewater treatment facilities. The reported effluent mercury concentrations were all less than 2,000 ng/L (EPA 2007).

Membrane filtration can be used in combination with a preceding treatment step. The upstream treatment is required to precipitate soluble mercury to a particulate form that can be removed through filtration. According to the EPA summary report, ultrafiltration is used to remove high-molecular weigh contaminants and solids (EPA 2007). The treatment effectiveness can depend on the source water quality since many constituents can cause membrane fouling, decreasing the effectiveness of the filters. One case study summarized in the EPA report showed that treatment of waste from a hazardous waste combustor treated with precipitation, sedimentation, and filtration achieved effluent mercury concentrations less than the detection limit of 200 ng/L.

Bench-scale research performed at the Oak Ridge Y-12 Plant in Tennessee evaluated the effectiveness of various adsorbents for removing mercury to below the NPDES limit of 12 ng/L and the potential revised limit of 51 ng/L (Hollerman et al. 1999). Several proprietary adsorbents were tested, including carbon, polyacrylate, polystyrene, and polymer adsorption materials. The adsorbents with thiol-based active sites were the most effective. Some of the adsorbents were able to achieve effluent concentrations less than 51 ng/L but none of the adsorbents achieved effluent concentrations less than 12 ng/L.

Bench-scale and pilot-scale testing performed on refinery wastewater was completed to determine treatment technology effectiveness for meeting very low mercury levels (Urgun-Demirtas, Benda, Gillenwater, Negri, Xiong & Snyder 2012) (Urgun-Demirtas, Negri, Gillenwater, Agwu Nnanna & Yu 2013). The Great Lakes Initiative water quality criterion for mercury is less than 1.3 ng/L for municipal and industrial wastewater plants in the Great Lakes region. This research included an initial bench scale test including membrane filtration, ultrafiltration, nanofiltration, and reverse osmosis to meet the mercury water quality criterion. The nanofiltration and reverse osmosis required increased pressures for filtration and resulted in increased mercury concentrations in the permeate. Based on this information and the cost difference between the filtration technologies, a pilot-scale test was performed. The 0.04 um PVDF GE ZeeWeed 500 series membranes were tested. The 1.3 ng/L water quality criterion was met under all pilot study operating conditions. The mercury in the refinery effluent was predominantly in particulate form which was well-suited for removal using membrane filtration.

Based on available data, it appears that existing municipal treatment facilities are capable of reducing effluent mercury to near the range of the proposed HHWQC on an average basis. Average effluent mercury in the range of 1.2 to 6.6 ng/L for existing facilities with secondary treatment and enhanced treatment with cloth filters and membranes. The Spokane County plant data range is an average of 1.2 ng/L to a maximum day of 3 ng/L. Addition of

advanced treatment processes such as GAC or RO would be expected to enhance removal rates. Data from the West Basin treatment facility in California suggests that at a detection limit of 7.99 ng/L mercury is not detected in the effluent from this advanced process train. A range of expected enhanced removal rates from the advanced treatment process trains might be expected to ranged from meeting the proposed standard at 5 ng/L to lower concentrations represented by the Spokane County performance level (membrane filtration) in the range of 1 to 3 ng/L, to perhaps even lower levels with additional treatment. For municipal plants in Washington, this would suggest that effluent mercury values from the two advanced treatment process alternatives might range from 1 to 5 ng/L (0.001 to 0.005 µg/L) and perhaps substantially better, depending upon RO and GAC removals. It is important to note that industrial plants may have higher existing mercury levels and thus the effluent quality that is achievable at an industrial facility would be of lower quality.

Summary of Mercury Technologies

The literature search revealed limited research on mercury removal technologies at the revised effluent limit of 0.005 µg/L. Tertiary filtration with membrane filters or reverse osmosis showed the best ability to achieve effluent criteria less than 0.005 µg/L.

4.2.3 Arsenic

A variety of treatment technologies can be applied to capture arsenic (Table 3). Most of the information in the technical literature and from the treatment technology vendors is focused on potable water treatment for compliance with a Safe Drinking Water Act (SDWA) maximum contaminant level (MCL) of 10 µg/L. The most commonly used arsenic removal method for a wastewater application (tertiary treatment) is coagulation/ flocculation plus filtration. This method by itself could remove more than 90 to 95 percent of arsenic. Additional post-treatment through adsorption, ion exchange, or reverse osmosis is required for ultra-low arsenic limits in the 0.018 µg/L range under consideration in the proposed rulemaking process. In each case it is recommended to perform pilot-testing of each selected technology.

Table 3: Summary of Arsenic Removal Technologies[1]

Technology	Advantages	Disadvantages
Coagulation/filtration	• Simple, proven technology • Widely accepted • Moderate operator training	• pH sensitive • Potential disposal issues of backwash waste • As^{+3} and As^{+5} must be fully oxidized
Lime softening	• High level arsenic treatment • Simple operation change for existing lime softening facilities	• pH sensitive (requires post treatment adjustment) • Requires filtration • Significant sludge operation
Adsorptive media	• High As^{+5} selectivity • Effectively treats water with high total dissolved solids (TDS)	• Highly pH sensitive • Hazardous chemical use in media regeneration • High concentration SeO_4^{-2}, F^-, Cl^-, and SO_4^{-2} may limit arsenic removal

Table 3: Summary of Arsenic Removal Technologies[1]

Technology	Advantages	Disadvantages
Ion exchange	• Low contact times • Removal of multiple anions, including arsenic, chromium, and uranium	• Requires removal of iron, manganese, sulfides, etc. to prevent fouling • Brine waste disposal
Membrane filtration	• High arsenic removal efficiency • Removal of multiple contaminants	• Reject water disposal • Poor production efficiency • Requires pretreatment

[1]Adapted from WesTech

The removal of arsenic in activated sludge is minimal (less than 20 percent) (Andrianisa et al. 2006), but biological treatment can control arsenic speciation. During aerobic biological process As (III) is oxidized to As (V). Coagulation/flocculation/filtration removal, as well as adsorption removal methods, are more effective in removal of As(V) vs. As (III). A combination of activated sludge and post-activated sludge precipitation with ferric chloride (addition to MLSS and effluent) results in a removal efficiency of greater than 95 percent. This combination could decrease As levels from 200 µg/L to less than 5 µg/L (5,000 ng/L) (Andrianisa et al. 2008) compared to the 0.018 µg/L range under consideration in the proposed rulemaking process.

Data from the West Basin facility (using MF/RO/AOP) suggests effluent performance in the range of 0.1 to 0.2 µg/L, but it could also be lower since a detection limit used there of 0.15 µg/l is an order of magnitude higher than the proposed HHWQC. A range of expected enhanced removal rates might be assumed to equivalent to that achieved at West Basin in 0.1 to 0.2 µg/L range.

Review of Specific Technologies for Arsenic Removal

Coagulation plus Settling or Filtration

Coagulation may remove more than 95 percent of arsenic through the creation of particulate metal hydroxides. Ferric sulfite is typically more efficient and applicable to most wastewater sources compared to alum. The applicability and extent of removal should be pilot-tested, since removal efficiency is highly dependent on the water constituents and water characteristics (i.e., pH, temperature, solids).

Filtration can be added after or instead of settling to increase arsenic removal. Example treatment trains with filtration are shown in Figures 1 and 2, respectively.

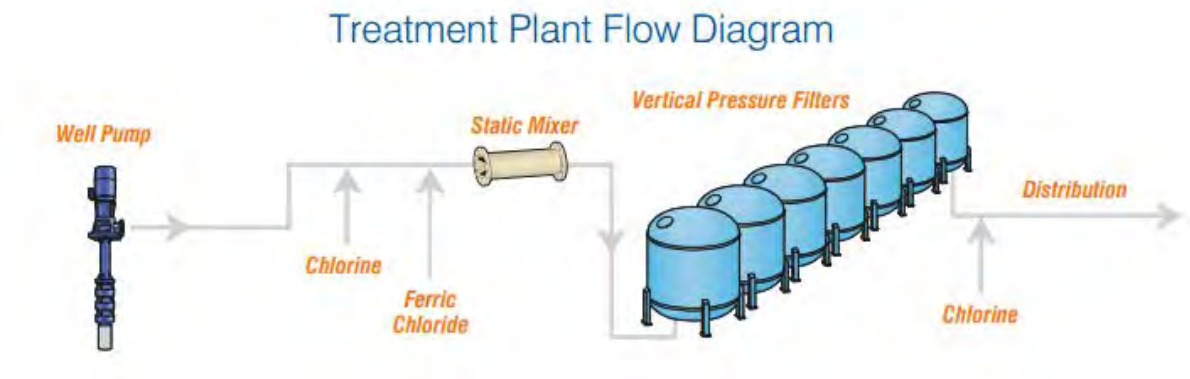

Figure 1. Water Treatment Configuration for Arsenic Removal (WesTech)

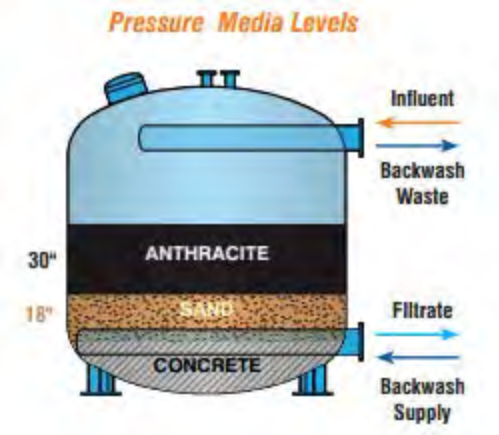

Figure 2. WesTech Pressure Filters for Arsenic Removal

One system for treatment of potable water with high levels of arsenic in Colorado (110 parts per million [ppm]) consists of enhanced coagulation followed by granular media pressure filters that include anthracite/silica sand/garnet media (WesTech). The arsenic levels were reduced to less than the drinking water MCL, which is 10 µg/L (10,000 ng/L). The plant achieves treatment by reducing the pH of the raw water to 6.8 using sulfuric acid, and then adding approximately 12 to 14 mg/L ferric sulfate. The water is filtered through 16 deep bed vertical pressure filters, the pH is elevated with hydrated lime and is subsequently chlorinated and fed into the distribution system.
(http://www.westechinc.com/public/uploads/global/2011/3/Fallon%20NV%20Installation%20ReportPressureFilter.pdf).

Softening (with lime)

Removes up to 90 percent arsenic through co-precipitation, but requires pH to be higher than 10.2.

Adsorption processes

Activated alumina is considered an adsorptive media, although the chemical reaction is an exchange of arsenic ions with the surface hydroxides on the alumina. When all the surface hydroxides on the alumina have been exchanged, the media must be regenerated. Regeneration consists of backwashing, followed by sodium hydroxide, flushing with water and neutralization with a strong acid. Effective arsenic removal requires sufficient empty bed contact time. Removal efficiency can also be impacted by the water pH, with neutral or slightly acidic conditions being considered optimum. If As (III) is present, it is generally advisable to increase empty bed contact time, as As (III) is adsorbed more slowly than As (V). Alumina dissolves slowly over time due to contact with the chemicals used for regeneration. As a result, the media bed is likely to become compacted if it is not backwashed periodically.

Granular ferric hydroxide works by adsorption, but when the media is spent it cannot be regenerated and must be replaced. The life of the media depends upon pH of the raw water, the concentrations of arsenic and heavy metals, and the volume of water treated daily. Periodic backwashing is required to prevent the media bed from becoming compacted and pH may need to be adjusted if it is high, in order to extend media life. For maximum arsenic removal, filters operate in series. For less stringent removal, filters can operate in parallel.

One type of adsorption media has been developed for application to non-drinking water processes for arsenic, phosphate and for heavy metals removal by sorption (Severent Trent Bayoxide® E IN-20). This granular ferric oxide media has been used for arsenic removal from

mining and industrial wastewaters, selenium removal from refinery wastes and for phosphate polishing of municipal wastewaters. Valley Vista drinking water treatment with Bayoxide® E IN-20 media achieves removal from 31-39 µg/L (31,000-39,000 ng/L) to below 10 µg/L MCL (http://www.severntrentservices.com/News/Successful_Drinking_Water_Treatment_in_an_Arsenic__Hot_Spot__nwMFT_452.aspx).

Another adsorptive filter media is greensand. Greensand is available in two forms: as glauconite with manganese dioxide bound ionically to the granules and as silica sand with manganese dioxide fused to the granules. Both forms operate in pressure filters and both are effective. Greensand with the silica sand core operates at higher water temperatures and higher differential pressures than does greensand with the glauconite core. Arsenic removal requires a minimum concentration of iron. If a sufficient concentration of iron is not present in the raw water, ferric chloride is added.

WesTech filters with greensand and permanganate addition for drinking water systems can reduce As from 15-25 µg/L to non-detect. Sodium hypochlorite and/or potassium permanganate are added to the raw water prior to the filters. Chemical addition may be done continuously or intermittently, depending on raw water characteristics. These chemicals oxidize the iron in the raw water and also maintain the active properties of the greensand itself. Arsenic removal is via co-precipitation with the iron.

Ion Exchange

Siemens offers a potable ion exchange (PIX) arsenic water filtration system. PIX uses ion exchange resin canisters for the removal of organic and inorganic contaminants, in surface and groundwater sources to meet drinking water standards.

Filtronics also uses ion exchange to treat arsenic. The technology allows removal for below the SWDA MCL for potable water of 10 µg/L (10,000 ng/L).

Reverse osmosis

Arsenic is effectively removed by RO when it is in oxidative state As(V) to approximately 1,000 ng/L or less (Ning 2002).

Summary of Arsenic Technologies

The current state of the technology for arsenic removal is at the point where all the processes target the SWDA MCL for arsenic in potable water. Current EPA maximum concentration level for drinking water is 10 ug/l; much higher than 0.0018 µg/L target for arsenic in this study. The majority of the methods discussed above are able to remove arsenic to either EPA maximum contaminant level or to the level of detection. The lowest detection limit of one of the EPA approved methods of arsenic measurements is 20 ng/l (0.020 µg/l) (Grosser, 2010), which is comparable to the 0.018 µg/L limit targeted in this study.

4.2.1 Polycyclic Aromatic Hydrocarbons

BAP During Biological Treatment

During wastewater treatment process, BAP tends to partition into sludge organic matter (Melcer et al. 1993). Primary and secondary processing could remove up to 60 percent of incoming PAHs and BAP in particular, mostly due to adsorption to sludge (Kindaichi et al., NA, Wayne et al. 2009). Biodegradation of BAP is expected to be very low since there are more than five benzene rings which are resistant to biological degradation. Biosurfactant addition to biological process could partially improve biodegradation, but only up to removal rates of 50 percent (Sponza et al. 2010). Existing data from municipal treatment facilities in Washington state have

influent and effluent concentrations of BAP of approximately 0.30 ng/L indicating that current secondary treatment has limited effectiveness at BAP removal.

Methods to Enhance Biological Treatment of BAP

Ozonation prior to biological treatment could potentially improve biodegradability of BAP (Zeng et al. 2000). In the case of soil remediation, ozonation before biotreatment improved biodegradation by 70 percent (Russo et al. 2012). The overall removal of BAP increased from 23 to 91 percent after exposure of water to 0.5 mg/L ozone for 30 minutes during the simultaneous treatment process and further to 100 percent following exposure to 2.5 mg/L ozone for 60 minutes during the sequential treatment mode (Yerushalmi et al. 2006). In general, to improve biodegradability of BAP, long exposure to ozone might be required (Haapea et al. 2006).

Sonication pre-treatment or electronic beam irradiation before biological treatment might also make PAHs more bioavailable for biological degradation..

Recent studies reported that a MBR is capable of removing PAHs from wastewater (Rodrigue and Reilly 2009; Gonzaleza et al. 2012). None of the studies listed the specific PAHs constituents removed.

Removal of BAP from Drinking Water

Activated Carbon

Since BAP has an affinity to particulate matter, it is removed from the drinking water sources by means of adsorption, such as granular activated carbon (EPA). Similarly, Oleszczuk et al. (2012) showed that addition of 5 percent activated carbon could remove 90 percent of PAHs from the wastewater.

Reverse Osmosis

Light (1981) (referenced by Williams, 2003) studied dilute solutions of PAHs, aromatic amines, and nitrosamines and found rejections of these compounds in reverse osmosis to be over 99 percent for polyamide membranes. Bhattacharyya et al. (1987) (referenced by Williams, 2003) investigated rejection and flux characteristics of FT30 membranes for separating various pollutants (PAHs, chlorophenols, nitrophenols) and found membrane rejections were high (>98 percent) for the organics under ionized conditions.

Summary of BAP Technologies

Current technologies show that BAP removal may be 90 percent or greater. The lowest detection limit for BAP measurements is 0.006 µg/L, which is also the assumed secondary effluent BAP concentration assumed for this study. If this assumption is accurate, it appears technologies may exist to remove BAP to a level below the proposed criteria applied as an effluent limit of 0.0013 µg/L; however, detection limits exceed this value and it is impossible to know this for certain. A municipal wastewater treatment plant study reported both influent and effluent BAP concentrations less than the HHWQC of 0.0013 ug/L (Ecology, 2010).

4.3 Unit Processes Evaluated

Based on the results of the literature review, a wide range of technologies were evaluated for toxic constituent removal. A listing of the technologies is as follows:

- Chemically enhanced primary treatment (CEPT): this physical and chemical technology is based on the addition of a metal salt to precipitate particles prior to primary treatment, followed by sedimentation of particles in the primary clarifiers. This technology has been

shown to effectively remove arsenic but there is little data supporting the claims. As a result, the chemical facilities are listed as optional.

- Activated sludge treatment (with a short SRT of approximately 8 days or less): this biological technology is commonly referred to as secondary treatment. It relies on converting dissolved organics into solids using biomass. Having a short SRT is effective at removing degradable organics referred to as BOD compounds for meeting existing discharge limits. Dissolved constituents with a high affinity to adsorb to biomass (e.g., metals, high molecular weight organics, and others) will be better removed compared to smaller molecular weight organics and recalcitrant compounds which will have minimal removal at a short SRT.
- Enhanced activated sludge treatment (with a long SRT of approximately 8 days or more): this technology builds on secondary treatment by providing a longer SRT, which enhances sorption and biodegradation. The improved performance is based on having more biomass coupled with a more diverse biomass community, especially nitrifiers, which have been shown to assist in removal of some of the more recalcitrant constituents not removed with a shorter SRT (e.g., lower molecular weight PAHs). There is little or no data available on the effectiveness of this treatment for removing BAP.

  Additional benefits associated with having a longer SRT are as follows:

  - Lower BOD/TSS discharge load to receiving water
  - Improved water quality and benefit to downstream users
  - Lower effluent nutrient concentrations which reduce algal growth potential in receiving waters
  - Reduced receiving water dissolved oxygen demand due to ammonia removal
  - Reduced ammonia discharge, which is toxic to aquatic species
  - Improved water quality for habitat, especially as it relates to biodiversity and eutrophication
  - Secondary clarifier effluent more conditioned for filtration and disinfection
  - Greater process stability from the anaerobic/anoxic zones serving as biological selectors
- Coagulation/Flocculation and Filtration: this two-stage chemical and physical process relies on the addition of a metal salt to precipitate particles in the first stage, followed by the physical removal of particles in filtration. This technology lends itself to constituents prone to precipitation (e.g., arsenic).
- Lime Softening: this chemical process relies on increasing the pH as a means to either volatilize dissolved constituents or inactivate pathogens. Given that none of the constituents being studied are expected to volatilize, this technology was not carried forward.
- Adsorptive Media: this physical and chemical process adsorbs constituents to a combination of media and/or biomass/chemicals on the media. There are several types of media, with the most proven and common being GAC. GAC can also serve as a coarse roughing filter.
- Ion Exchange: this chemical technology exchanges targeted constituents with a resin. This technology is common with water softeners where the hard divalent cations are

exchanged for monovalent cations to soften the water. Recently, resins that target arsenic and mercury removal include activated alumina and granular ferric hydroxides have been developed. The resin needs to be cleaned and regenerated, which produces a waste slurry that requires subsequent treatment and disposal. As a result, ion exchange was not considered for further.

- Membrane Filtration: This physical treatment relies on the removal of particles larger than the membranes pore size. There are several different membrane pore sizes as categorized below.
  - Microfiltration (MF): nominal pore size range of typically between 0.1 to 1 micron. This pore size targets particles, both inert and biological, and bacteria. If placed in series with coagulation/flocculation upstream, dissolved constituents precipitated out of solution and bacteria can be removed by the MF membrane.
  - Ultrafiltration (UF): nominal pore size range of typically between 0.01 to 0.1 micron. This pore size targets those solids removed with MF (particles and bacteria) plus viruses and some colloidal material. If placed in series with coagulation/flocculation upstream, dissolved constituents precipitated out of solution can be removed by the UF membrane.
  - Nanofiltration (NF): nominal pore size range of typically between 0.001 to 0.010 micron. This pore size targets those removed with UF (particles, bacteria, viruses) plus colloidal material. If placed in series with coagulation/flocculation upstream, dissolved constituents precipitated out of solution can be removed by the NF membrane.
- MBR (with a long SRT): this technology builds on secondary treatment whereby the membrane (microfiltration) replaces the secondary clarifier for solids separation. As a result, the footprint is smaller, the mixed liquor suspended solids concentration can be increased to about 5,000 – 10,000 mg/L, and the physical space required for the facility reduced when compared to conventional activated sludge. As with the activated sludge option operated at a longer SRT, the sorption and biodegradation of organic compounds are enhanced in the MBR process. The improved performance is based on having more biomass coupled with a more diverse biomass community, especially nitrifiers which have been shown to assist in removal of persistent dissolved compounds (e.g., some PAHs). There is little or no data available on effectiveness at removing BAP. Although a proven technology, MBRs were not carried further in this technology review since they are less likely to be selected as a retrofit for an existing activated sludge (with a short SRT) secondary treatment facility. The MBR was considered to represent a treatment process approach more likely to be selected for a new, greenfield treatment facility. Retrofits to existing secondary treatment facilities can accomplish similar process enhancement by extending the SRT in the activated sludge process followed by the addition of tertiary membrane filtration units.
- RO: This physical treatment method relies on the use of sufficient pressure to osmotically displace water across the membrane surface while simultaneously rejecting most salts. RO is very effective at removing material smaller than the size ranges for the membrane filtration list above, as well as salts and other organic compounds. As a result, it is expected to be more effective than filtration and MBR methods described above at removing dissolved constituents. Although effective, RO produces a brine reject water that must be managed and disposed.

- Advanced Oxidation Processes (AOPs): this broad term considers all chemical and physical technologies that create strong hydroxyl-radicals. Examples of AOPs include Fenton's oxidation, ozonation, ultraviolet/hydrogen peroxide (UV-H2O2), and others. The radicals produced are rapid and highly reactive at breaking down recalcitrant compounds. Although effective at removing many complex compounds such as those evaluated in this study, AOPs does not typically have as many installations as membranes and activated carbon technologies. As a result, AOPs were not carried forward.

Based on the technical literature review discussed above, a summary of estimated contaminant removal rated by unit treatment process is presented in Table 4.

Table 4. Contaminants Removal Breakdown by Unit Process

Unit Process	Arsenic	BAP	Mercury	Polychlorinated Biphenyls
Activated Sludge Short SRT	No removal	Partial Removal by partitioning		80% removal; effluent <0.88 ng/L
Activated Sludge Long SRT	No removal	Partial removal by partitioning and/or partially biodegradation; MBR could potentially remove most of BAP		>90% removal with a membrane bioreactor, <0.04 ng/L (includes membrane filtration)
Membrane Filtration (MF)	More than 90 % removal (rejection of bound arsenic)	No removal	<1.3 ng/L	>90% removal with a membrane bioreactor, <0.04 ng/L (includes membrane filtration)
Reverse Osmosis (RO)	More than 90% removal (rejection of bound arsenic and removal of soluble arsenic)	More than 98% removal		
Granular Activated Carbon (GAC)	No removal, removal only when carbon is impregnated with iron	90 % removal	<300 ng/L (precipitation and carbon adsorption) <51 ng/L (GAC)	<800 ng/L Likely requires upstream filtration
Disinfection	--	--	--	--

4.4 Unit Processes Selected

The key conclusion from the literature review was that there is limited, to no evidence, that existing treatment technologies are capable of simultaneously meeting all four of the revised discharge limits for the toxics under consideration. Advanced treatment using RO or GAC is expected to provide the best overall removal of the constituents of concern. It is unclear whether these advanced technologies are able to meet revised effluent limits, however these processes may achieve the best effluent quality of the technologies reviewed. This limitation in the findings is based on a lack of an extensive dataset on treatment removal effectiveness in the technical literature for the constituents of interest at the low levels relevant to the proposed criteria, which

approach the limits of reliable removal performance for the technologies. As Table 4 highlights, certain unit processes are capable of removing a portion, or all, of the removal requirements for each technology. The removal performance for each constituent will vary from facility to facility and require a site-specific, detailed evaluation because the proposed criteria are such low concentrations. In some cases, a facility may only have elevated concentrations of a single constituent of concern identified in this study. In other cases, a discharger may have elevated concentrations of the four constituents identified in this study, as well as others not identified in this study but subject to revised water quality criteria. This effort is intended to describe a planning level concept of what treatment processes are required to comply with discharge limits for all four constituents. Based on the literature review of unit processes above, two different treatment trains were developed for the analysis that are compared against a baseline of secondary treatment as follows:

- Baseline: represents conventional secondary treatment that is most commonly employed nationwide at wastewater treatment plants. A distinguishing feature for this treatment is the short solids residence time (SRT) (<8 days) is intended for removal of BOD with minimal removal for the toxic constituents of concern.
- Advanced Treatment – MF/RO: builds on baseline with the implementation of a longer SRT (>8 days) and the addition of MF and RO. The longer SRT not only removes BOD, but it also has the capacity to remove nutrients and a portion of the constituents of concern. This alternative requires a RO brine management strategy which will be discussed in sub-sections below.
- Advanced Treatment – MF/GAC: this alternative provides a different approach to advanced treatment with MF/RO by using GAC and avoiding the RO reject brine water management concern. Similar to the MF/RO process, this alternative has the longer SRT (>8 days) with the capacity to remove BOD, nutrients, and a portion of the toxic constituents of concern. As a result, the decision was made to develop costs for both advanced treatment options.

A description of each alternative is provided in Table 5. The process flowsheets for each alternative are presented in Figure 3 to Figure 5.

4.4.1 Baseline Treatment Process

A flowsheet of the baseline treatment process is provided in Figure 3. The baseline treatment process assumes the current method of treatment commonly employed by dischargers. For this process, water enters the headworks and undergoes primary treatment, followed by conventional activated sludge (short SRT) and disinfection. The solids wasted in the activated sludge process are thickened, followed by mixing with primary solids prior to entering the anaerobic digestion process for solids stabilization. The digested biosolids are dewatered to produce a cake and hauled off-site. Since the exact process for each interested facility in Washington is unique, this baseline treatment process was used to establish the baseline capital and O&M costs. The baseline costs will be compared against the advanced treatment alternatives to illustrate the magnitude of the increased costs and environmental impacts.

Table 5. Unit Processes Description for Each Alternative

Unit Process	Baseline	Advanced Treatment – MF/RO	Advanced Treatment - GAC
Influent Flow	5 mgd	5 mgd	5 mgd
Chemically Enhanced Primary Treatment (CEPT); Optional	--	• Metal salt addition (alum) upstream of primaries	• Metal salt addition (alum) upstream of primaries
Activated Sludge	• Hydraulic Residence Time (HRT): 6 hrs • Short Solids Residence Time (SRT): <8 days	• Hydraulic Residence Time (HRT): 12 hrs (Requires more tankage than the Baseline) • Long Solids Residence Time (SRT): >8 days (Requires more tankage than the Baseline)	• Hydraulic Residence Time (HRT): 12 hrs (Requires more tankage than the Baseline) • Long Solids Residence Time (SRT): >8 days (Requires more tankage than the Baseline)
Secondary Clarifiers	Hydraulically Limited	Solids Loading Limited (Larger clarifiers than Baseline)	Solids Loading Limited (Larger clarifiers than Baseline)
Microfiltration (MF)	--	Membrane Filtration to Remove Particles and Bacteria	Membrane Filtration to Remove Particles and Bacteria
Reverse Osmosis (RO)	--	Treat 50% of the Flow by RO to Remove Metals and Dissolved Constituents. Sending a portion of flow through the RO and blending it with the balance of plant flows ensures a stable non-corrosive, non-toxic discharge.	--
Reverse Osmosis Brine Reject Mgmt	--	Several Options (All Energy or Land Intensive)	--
Granular Activated Carbon (GAC)	--	--	Removes Dissolved Constituents
Disinfection	Not shown to remove any of the constituents	Not shown to remove any of the constituents	Not shown to remove any of the constituents

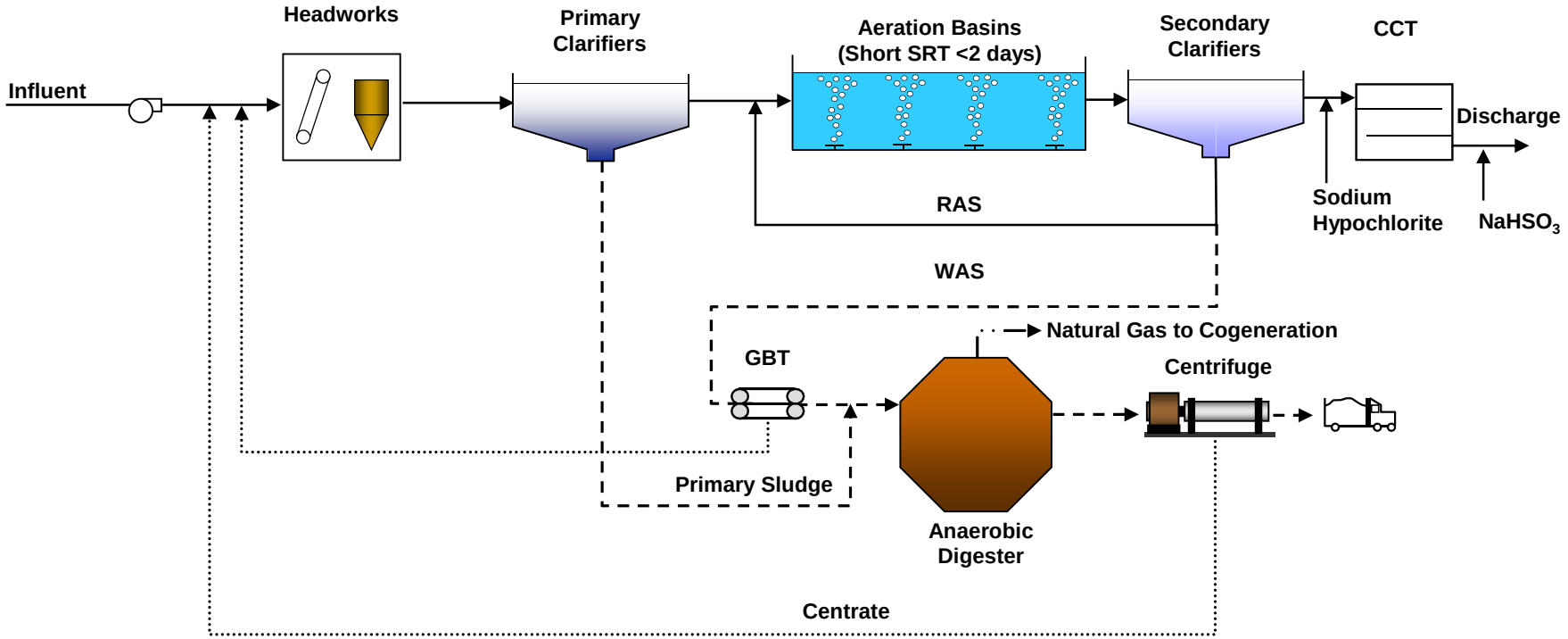

Figure 3. Baseline Flowsheet – Conventional Secondary Treatment

4.4.2 Advanced Treatment – MF/RO Alternative

A flowsheet of the advanced treatment – MF/RO alternative is provided in Figure 4. This alternative builds on the baseline secondary treatment facility, whereby the SRT is increased in the activated sludge process, and MF and RO are added prior to disinfection. The solids treatment train does not change with respect to the baseline. Additionally, a brine management strategy must be considered.

The RO process concentrates contaminants into a smaller volume reject stream. Disposing of the RO reject stream can be a problem because of the potentially large volume of water involved and the concentration of contaminants contained in the brine. For reference, a 5 mgd process wastewater flow might result in 1 mgd of brine reject requiring further management. The primary treatment/handling options for RO reject are as follows:

- Zero liquid discharge
- Surface water discharge
- Ocean discharge
- Haul and discharge to coastal location for ocean discharge
- Sewer discharge
- Deep well injection
- Evaporate in a pond
- Solar pond concentrator

Many of the RO brine reject management options above result in returning the dissolved solids to a “water of the state” such as surface water, groundwater, or marine waters. Past rulings in Washington State have indicated that once pollutants are removed from during treatment they are not to be re-introduced to a water of the state. As a result, technologies with this means for disposal were not considered viable options for management of RO reject water in Washington.

Zero Liquid Discharge

Zero liquid discharge (ZLD) is a treatment process that produces a little or no liquid brine discharge but rather a dried residual salt material. This process improves the water recovery of the RO system by reducing the volume of brine that must be treated and disposed of in some manner. ZLD options include intermediate treatment, thermal-based technologies, pressure driven membrane technologies, electric potential driven membrane technologies, and other alternative technologies.

Summary

There are many techniques which can be used to manage reject brine water associated with RO treatment. The appropriate alternative is primarily governed by geographic and local constraints. A comparison of the various brine management methods and potential costs are provided in Table 6.

Of the listed options, ZLD was considered for this analysis as the most viable approach to RO reject water management. An evaporation pond was used following ZLD. The strength in this combination is ZLD reduces the brine reject volume to treat, which in turn reduces the required evaporation pond footprint. The disadvantage is that evaporation ponds require a substantial amount of physical space which may not be available at existing treatment plant sites. It is also important to recognize that the greenhouse gas (GHG) emissions vary widely for the eight brine management options listed above based on energy and chemical intensity.

Table 6. Brine Disposal Method Relative Cost Comparison

Disposal Method	Description	Relative Capital Cost	Relative O&M Cost	Comments
Zero Liquid Discharge (ZLD)	Further concentrates brine reject for further downstream processing	High	High	This option is preferred as an intermediate step. This rationale is based on the reduction in volume to handle following ZLD. For example, RO reject stream volume is reduced on the order of 50-90%.
Surface Water Discharge	Brine discharge directly to surface water. Requires an NPDES permit.	Lowest	Lowest	Both capital and O&M costs heavily dependent on the distance from brine generation point to discharge. Not an option for nutrient removal.
Ocean Discharge	Discharge through a deep ocean outfall.	Medium	Low	Capital cost depends on location and availability of existing deep water outfall.
Sewer Discharge	Discharge to an existing sewer pipeline for treatment at a wastewater treatment plant.	Low	Low	Both capital and O&M costs heavily dependent on the brine generation point to discharge distance. Higher cost than surface water discharge due to ongoing sewer connection charge. Not an option for wastewater treatment.
Deep Well Injection	Brine is pumped underground to an area that is isolated from drinking water aquifers.	Medium	Medium	Technically sophisticated discharge and monitoring wells required. O&M cost highly variable based on injection pumping energy.
Evaporation Ponds	Large, lined ponds are filled with brine. The water evaporates and a concentrated salt remains.	Low – High	Low	Capital cost highly dependent on the amount and cost of land.
Salinity Gradient Solar Ponds (SGSP)	SGSPs harness solar power from pond to power an evaporative unit.	Low – High	Lowest	Same as evaporation ponds plus added cost of heat exchanger and pumps. Lower O&M cost due to electricity production.
Advanced Thermal Evaporation	Requires a two-step process consisting of a brine concentrator followed by crystallizer	High	Highest	Extremely small footprint, but the energy from H_2O removal is by far the most energy intensive unless waste heat is used.

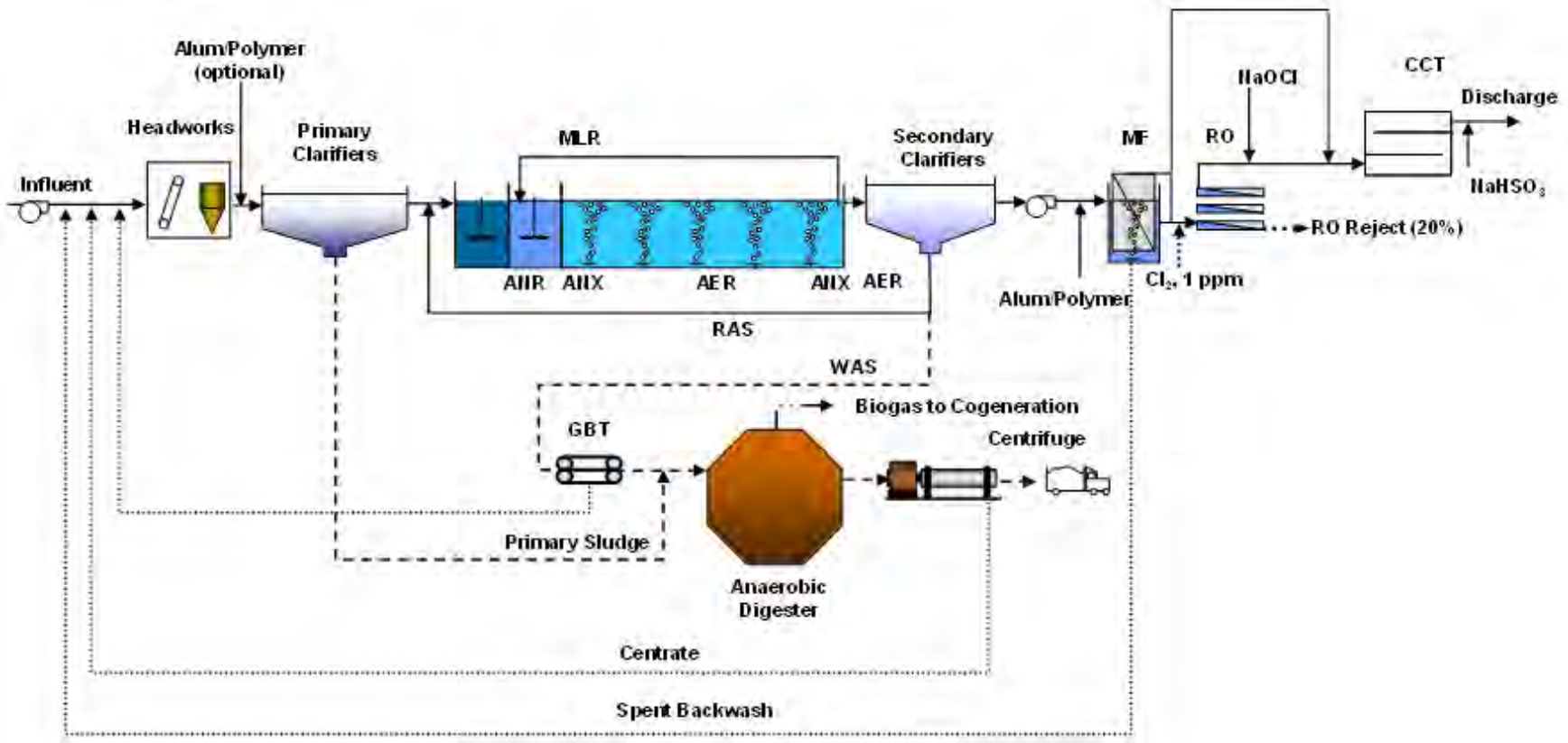

Figure 4. Advanced Treatment Flowsheet – Tertiary Microfiltration and Reverse Osmosis

4.4.3 Advanced Treatment – MF/GAC Alternative

A flowsheet of the advanced treatment – MF/GAC alternative is provided in Figure 5. Following the MF technology, a GAC contactor and media are required.

This alternative was developed as an option that does not require a brine management technology (e.g., ZLD) for comparison to the MF/RO advanced treatment alternative. However, this treatment alternative does require that the GAC be regenerated. A baseline secondary treatment facility can be retrofitted for MF/GAC. If an existing treatment facility has an extended aeration lagoon, the secondary effluent can be fed to the MF/GAC. The longer SRT in the extended aeration lagoon provides all the benefits associated with the long SRT in an activated sludge plant as previously stated:

- Lower BOD/TSS discharge load
- Higher removal of recalcitrant constituents and heavy metals
- Improved water quality and benefit to downstream users
- Less downstream algal growth
- Reduced receiving water dissolved oxygen demand due to ammonia removal
- Reduced ammonia discharge loads, which is toxic to several aquatic species
- Improved water quality for habitat, especially as it relates to biodiversity and eutrophication
- Secondary clarifier effluent more conditioned for filtration and disinfection
- Greater process stability from the anaerobic/anoxic zones serving as a selector

If an existing treatment facility employs a high rate activated sludge process (short SRT) similar to the baseline, it is recommended that the activated sludge process SRT be increased prior to the MF/GAC unit processes. The longer SRT upstream of the MF is preferred to enhance the membrane flux rate, reduce membrane biofouling, increase membrane life, and reduce the chemicals needed for membrane cleaning.

The key technical and operational challenges associated with the tertiary add-on membrane filtration units are as follows:

- The membrane filtration technology is a proven and reliable technology. With over 30 years of experience, it has made the transition in recent years from an emerging technology to a proven and reliable technology.
- Membrane durability dependent on feed water quality. The water quality is individual facility specific.
- Membranes are sensitive to particles, so upstream screening is critical. The newer generations of membranes have technical specifications that require a particular screen size.
- Membrane area requirements based on peak flows as water must pass through the membrane pores. Additionally, membranes struggle with variable hydraulic loading. Flow equalization upstream can greatly reduce the required membrane surface area and provide uniform membrane loading.

- Membrane tanks can exacerbate any foam related issues from the upstream biological process. Foam entrapment in the membrane tank from the upstream process can reduce membrane filtration capacity and in turn result in a plant-wide foam problem.
- Reliable access to the membrane modules is key to operation and maintenance. Once PLC is functionary properly, overall maintenance requirements for sustained operation of the system are relatively modest.
- The membranes go through frequent membrane relaxing or back pulse and a periodic deep chemical clean in place (CIP) process.
- Sizing of membrane filtration facilities governed by hydraulic flux. Municipal wastewaters have flux values that range from about 20 to 40 gallons per square foot per day (gfd) under average annual conditions. The flux associated with industrial applications is wastewater specific.

Following the MF is the activated carbon facilities. There are two kinds of activated carbon used in treating water: powdered activated carbon (PAC) and GAC. PAC is finely-ground, loose carbon that is added to water, mixed for a short period of time, and removed. GAC is larger than PAC, is generally used in beds or tanks that permit higher adsorption and easier process control than PAC allows, and is replaced periodically. PAC is not selective, and therefore, will adsorb all active organic substances making it an impractical solution for a wastewater treatment plant. As a result, GAC was considered for this analysis. The type of GAC (e.g., bituminous and subbituminous coal, wood, walnut shells, lignite or peat), gradation, and adsorption capacity are determined by the size of the largest molecule/ contaminant that is being filtered (AWWA, 1990).

As water flows through the carbon bed, contaminants are captured by the surfaces of the pores until the carbon is no longer able to adsorb new molecules. The concentration of the contaminant in the treated effluent starts to increase. Once the contaminant concentration in the treated water reaches an unacceptable level (called the breakthrough concentration), the carbon is considered "spent" and must be replaced by virgin or reactivated GAC.

The capacity of spent GAC can be restored by thermal reactivation. Some systems have the ability to regenerate GAC on-site, but in general, small systems haul away the spent GAC for off-site regeneration (EPA 1993). For this study, off-site regeneration was assumed.

The basic facilities and their potential unit processes included in this chapter are as follows:

- GAC supply and delivery
- Influent pumping
  - Low head feed pumping
  - High head feed pumping (assumed for this study as we have low limits so require high beds)
- Contactors and backwash facilities
  - Custom gravity GAC contactor
  - Pre-engineered pressure GAC contactor (Used for this study)
  - Backwash pumping
- GAC transport facilities
  - Slurry pumps
  - Eductors (Used for this study)

- Storage facilities
  - Steel tanks
  - Concrete tanks (Used for this study; larger plants would typically select concrete tanks)
- Spent carbon regeneration
  - On-site GAC regeneration
  - Off-Site GAC regeneration

Following the MF is the GAC facility. The GAC contactor provides about a 12-min hydraulic residence time for average annual conditions. The GAC media must be regenerated about twice per year in a furnace. The constituents sorbed to the GAC media are removed during the regeneration process. A typical design has full redundancy and additional storage tankage for spent and virgin GAC. Facilities that use GAC need to decide whether they will regenerate GAC on-site or off-site. Due to challenges associated with receiving air emission permits for new furnaces, it was assumed that off-site regeneration would be evaluated.

The key technical and operational challenges associated with the tertiary add-on GAC units are as follows:

- Nearest vendor to acquire virgin GAC – How frequently can they deliver virgin GAC and what are the hauling costs?
- Contactor selection is typically based on unit cost and flow variation. The concrete contactor is typically more cost effective at higher flows so it was used for this evaluation. The pre-engineered pressure contactor can handle a wider range of flows than a concrete contactor. Additionally, a pressure system requires little maintenance as they are essentially automated
- Periodical contactor backwashing is critical for maintaining the desired hydraulics and control biological growth
- Eductors are preferred over slurry pumps because they have fewer mechanical components. Additionally, the pump with eductors is not in contact with the carbon, which reduces wear.
- Off-site GAC regeneration seems more likely due to the challenges with obtaining an air emissions permit.

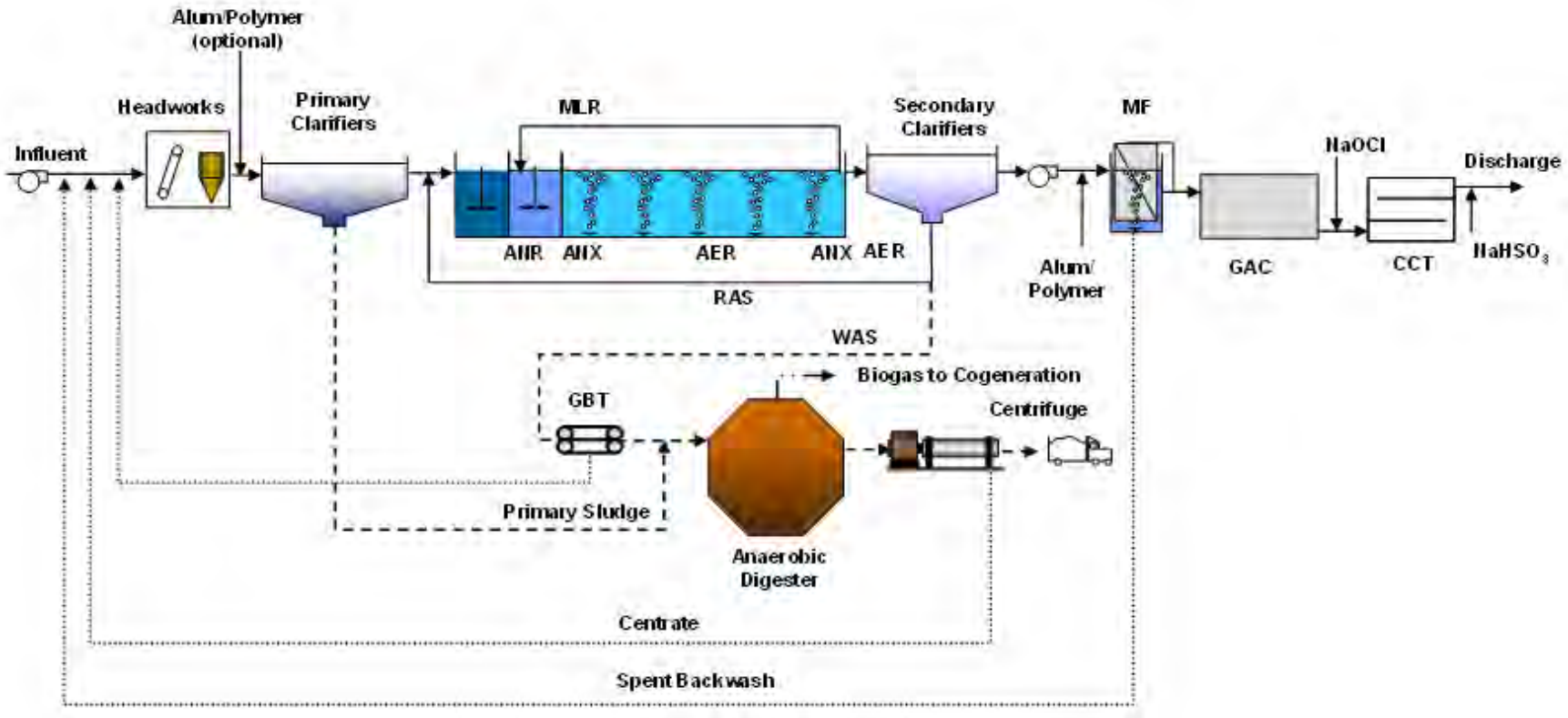

Figure 5. Advanced Treatment Flowsheet – Tertiary Microfiltration and Granular Activated Carbon

4.5 Steady-State Mass Balance

HDR used its steady-state mass balance program to calculate the flows and loads within the candidate advanced treatment processes as a means to size facilities. The design of wastewater treatment facilities are generally governed by steady-state mass balances. For a steady-state mass balance, the conservation of mass is calculated throughout the entire wastewater treatment facility for defined inputs. Dynamic mass balance programs exist for designing wastewater facilities, but for a planning level study such as this, a steady state mass balance program is adequate. A dynamic program is generally used for detailed design and is site-specific with associated requirements for more detailed wastewater characterization.

The set of model equations used to perform a steady-state mass balance are referred to as the model. The model equations provide a mathematical description of various wastewater treatment processes, such as an activated sludge process, that can be used to predict unit performance. The program relies on equations for each unit process to determine the flow, load, and concentration entering and leaving each unit process.

An example of how the model calculates the flow, load, and concentration for primary clarifiers is provided below. The steady-state mass balance equation for primary clarifiers has a single input and two outputs as shown in the simplified Figure 6. The primary clarifier feed can exit the primary clarifiers as either effluent or sludge. Solids not removed across the primaries leave as primary effluent, whereas solids captured leave as primary sludge. Scum is not accounted for.

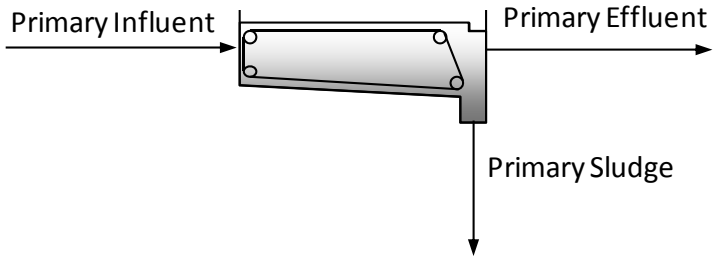

Figure 6. Primary Clarifier Inputs/Outputs

The mass balance calculation requires the following input:

- Solids removal percentage across the primaries (based on average industry accepted performance)
- Primary solids thickness (i.e., percent solids) (based on average industry accepted performance)

The steady-state mass balance program provides a reasonable first estimate for the process performance, and an accurate measure of the flows and mass balances at various points throughout the plant. The mass balance results were used for sizing the facility needs for each alternative. A listing of the unit process sizing criterion for each unit process is provided in Appendix A. By listing the unit process sizing criteria, a third-party user could redo the analysis and end up with comparable results. The key sizing criteria that differ between the baseline and treatment alternatives are as follows:

- Aeration basin mixed liquor is greater for the advanced treatment alternatives which in turn requires a larger volume
- The secondary clarifiers are sized based on hydraulic loading for the baseline versus solids loading for the advanced treatment alternatives

- The MF/GAC and MF/RO sizing is only required for the respective advanced treatment alternatives.

4.6 Adverse Environmental Impacts Associated with Advanced Treatment Technologies

The transition from the baseline (conventional secondary treatment) to either advanced treatment alternatives has some environmental impacts that merit consideration, including the following:

- Land area for additional system components (which for constrained facility sites, may necessitate land acquisition and encroachment into neighboring properties with associated issues and challenges, etc.).
- Increased energy use and atmospheric emissions of greenhouse gases and criteria air contaminants associated with power generation to meet new pumping requirements across the membrane filter systems (MF and RO) and GAC.
- Increased chemical demand associated with membrane filters (MF and RO).
- Energy and atmospheric emissions associated with granulated charcoal regeneration.
- RO brine reject disposal. The zero liquid discharge systems are energy intensive energy and increase atmospheric emissions as a consequence of the electrical power generation required for removing water content from brine reject.
- Increase in sludge generation while transitioning from the baseline to the advanced treatment alternatives. There will be additional sludge captured with the chemical addition to the primaries and membrane filters (MF and RO). Additionally, the GAC units will capture more solids.
- Benefits to receiving water quality by transitioning from a short SRT (<2 days) in the baseline to a long SRT (>8 days) for the advanced treatment alternatives (as previously stated):
    - Lower BOD/TSS discharge load
    - Higher removal of recalcitrant constituents and heavy metals
    - Improved water quality and benefit to downstream users
    - Reduced nutrient loadings to receiving waters and lower algal growth potential
    - Reduced receiving water dissolved oxygen demand due to ammonia removal
    - Reduced ammonia discharge loads, which is toxic to aquatic species
    - Improved water quality for habitat, especially as it relates to biodiversity and eutrophication
    - Secondary clarifier effluent better conditioned for subsequent filtration and disinfection
    - Greater process stability from the anaerobic/anoxic zones serving as a biological selectors

HDR calculated GHG emissions for the baseline and advanced treatment alternatives. The use of GHG emissions is a tool to normalize the role of energy, chemicals, biosolids hauling, and fugitive emissions (e.g., methane) in a single unit. The mass balance results were used to quantify energy demand and the corresponding GHG emissions for each alterative. Energy

demand was estimated from preliminary process calculations. A listing of the energy demand for each process stream, the daily energy demand, and the unit energy demand is provided in Table 7. The advanced treatment options range from 2.3 to 4.1 times greater than the baseline. This large increase in energy demand is attributed to the energy required to pass water through the membrane barriers and/or the granular activated carbon. Additionally, there is energy required to handle the constituents removed as either regenerating the GAC or handling the RO brine reject water. This additional energy required to treat the removed constituents is presented in Table 7.

Table 7. Energy Breakdown for Each Alternative (5 mgd design flow)

Parameter	Units	Baseline	Advanced Treatment – MF/GAC	Advanced Treatment – MF/RO
Daily Liquid Stream Energy Demand	MWh/d	11.6	23.8	40.8
Daily Solids Stream Energy Demand	MWh/d	-1.6	-1.1	-1.1
Daily Energy Demand	MWh/d	10.0	22.7	39.7
Unit Energy Demand	kWh/MG Treated	2,000	4,500	7,900

MWh/d = megawatt hours per day
kWh/MG = kilowatt hours per million gallons

Details on the assumptions used to convert between energy demand, chemical demand and production, as well as biologically-mediated gases (i.e., CH4 and N2O) and GHG emissions are provided in Appendix B.

A plot of the GHG emissions for each alternative is shown in Figure 7. The GHG emissions increase from the baseline to the two advanced treatment alternatives. The GHG emissions increase about 50 percent with respect to baseline when MF/GAC is used and the GHG emissions increase over 100 percent with respect to baseline with the MF/RO advanced treatment alternative.

The MF/GAC energy demand would be larger if GAC regeneration was performed on-site. The GHG emissions do not include the energy or air emissions that result from off-site GAC regeneration. Only the hauling associated with moving spent GAC is included. The energy associated with operating the furnace would exceed the GHG emissions from hauling spent GAC.

The zero liquid discharge in the MF/RO alternative alone is comparable to the Baseline. This contribution to increased GHG emissions by zero liquid discharge brine system highlights the importance of the challenges associated with managing brine reject.

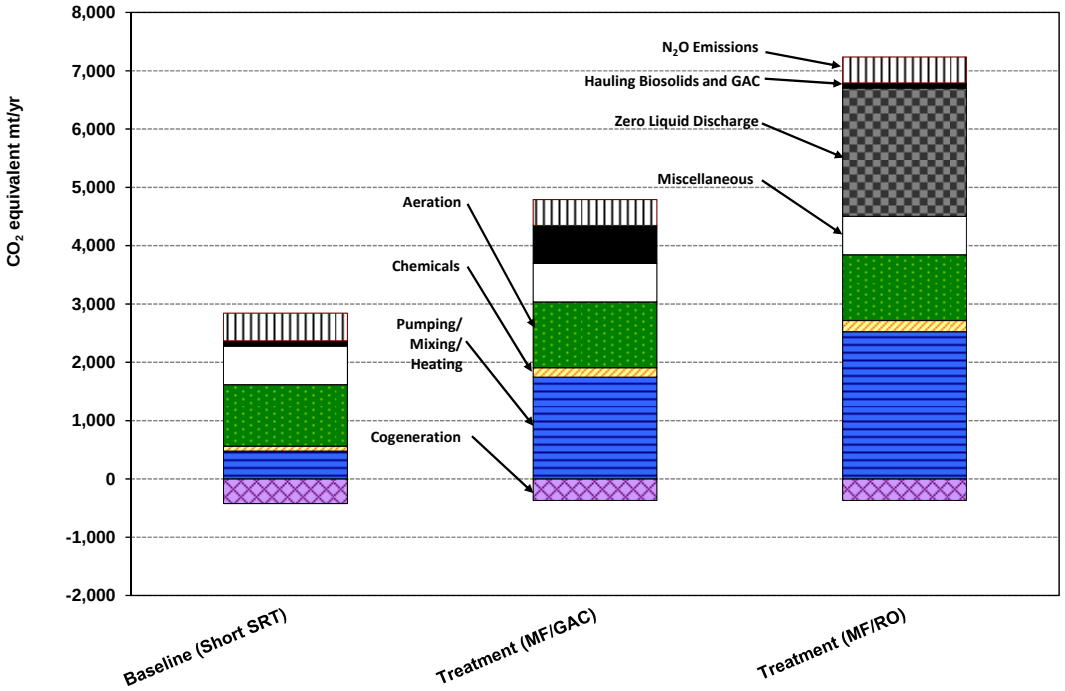

Figure 7. Greenhouse Gas Emissions for Each Alternative

The use of GHG emissions as a measure of sustainability does not constitute a complete comparison between the baseline and advanced treatment alternatives. Rather, it is one metric that captures the impacts of energy, chemical demand and production, as well as biologically-mediated gases (i.e., CH_4 and N_2O). The other environmental impacts of advanced treatment summarized in the list above should also be considered in decision making beyond cost analysis.

4.7 Costs

Total project costs along with the operations and maintenance costs were developed for each advanced treatment alternative for a comparison with baseline secondary treatment.

4.7.1 Approach

The cost estimates presented in this report are planning level opinions of probable construction costs for a nominal 5 mgd treatment plant design flow representing a typical facility without site specific details about local wastewater characteristics, physical site constraints, existing infrastructure, etc. The cost estimates are based on wastewater industry cost references, technical studies, actual project cost histories, and professional experience. The costs presented in this report are considered planning level estimates. A more detailed development of the advanced treatment process alternatives and site specific information would be required to further refine the cost estimates. Commonly this is accomplished in the preliminary design phase of project development for specific facilities following planning.

The cost opinion includes a range of costs associated with the level of detail used in this analysis. Cost opinions based on preliminary engineering can be expected to follow the Association for the Advancement of Cost Engineering (AACE International) Recommended Practice No. 17R-97 Cost Estimate Classification System estimate Class 4. A Class 4 estimate is based upon a 5 to 10 percent project definition and has an expected accuracy range of -30 to +50 percent and typical end usage of budget authorization and cost control. It is considered an

"order-of-magnitude estimate." The life-cycle costs were prepared using the net present value (NPV) method.

The cost associated for each new unit process is based on a unit variable, such as required footprint, volume, demand (e.g., lb O_2/hr), and others. This approach is consistent with the approach developed for the EPA document titled "Estimating Water Treatment Costs: Volume 2-Cost Curves Applicable to 1 to 200 mgd Treatment Plants" dated August 1979. The approach has been updated since 1979 to account for inflation and competition, but the philosophy for estimating costs for unit processes has not changed. For example, the aeration system sizing/cost is governed by the maximum month airflow demand. Additionally, the cost associated constructing an aeration basin is based on the volume. The cost considers economies of scale.

The O&M cost estimates were calculated from preliminary process calculations. The operations cost includes energy and chemical demand. For example, a chemical dose was assumed based on industry accepted dosing rates and the corresponding annual chemical cost for that particular chemical was accounted for. The maintenance values only considered replacement equipment, specifically membrane replacement for the Advanced Treatment Alternatives.

4.7.2 Unit Cost Values

The life-cycle cost evaluation was based on using the economic assumptions shown in Table 8. The chemical costs were based on actual values from other projects. To perform detailed cost evaluations per industry, each selected technology would need to be laid out on their respective site plan based on the location of the existing piping, channels, and other necessary facilities.

Table 8. Economic Evaluation Variables

Item	Value
Nominal Discount Rate	5%
Inflation Rate:	
General	3.5%
Labor	3.5%
Energy	3.5%
Chemical	3.5%
Base Year	2013
Project Life	25 years
Energy	$0.06/kWh
Natural Gas	$0.60/therm
Chemicals:	
Alum	$1.1/gal
Polymer	$1.5/gal
Hypochlorite	$1.5/gal
Salt	$0.125/lb
Antiscalant	$12.5/lb
Acid	$0.35/lb
Deionized Water	$3.75/1,000 gal
Hauling:	

Table 8. Economic Evaluation Variables

Item	Value
Biosolids Hauling Distance	100 miles (one way)
Biosolids Truck Volume	6,000 gal/truck
Biosolids Truck Hauling	$250/truck trip
GAC Regeneration Hauling Distance	250 miles (round trip)
GAC Regeneration Truck Volume	$20,000 lb GAC/truck
GAC Regeneration Truck Hauling	Included in cost of Virgin GAC

kWh= kilowatt hours; lbs=pounds; GAC=granulated activated carbon; gal=gallon

4.7.3 Net Present Value of Total Project Costs and Operations and Maintenance Cost in 2013 Dollars

An estimate of the net present value for the baseline treatment process and the incremental cost to implement the advanced treatment alternatives is shown in Table 9. The cost for the existing baseline treatment process was estimated based on new construction for the entire conventional secondary treatment process (Figure 3). The incremental cost to expand from existing baseline secondary treatment to advanced treatment was calculated by taking the difference between the baseline and the advanced treatment alternatives. These values serve as a benchmark for understanding the prospective cost for constructing advanced treatment at the planning level of process development.

Table 9. Treatment Technology Total Project Costs in 2013 Dollars for a 5 mgd Facility

Alternative	Total Construction Cost, 2013 dollars ($ Million)	O&M Net Present Value, 2013 dollars ($ Million)*	Total Net Present Value, 2013 dollars ($ Million)	NPV Unit Cost, 2013 dollars ($/gpd)
Baseline (Conventional Secondary Treatment)*	59 - 127	5 - 11	65 – 138	13 - 28
Advanced Treatment – MF/RO**	108 - 231	31 - 67	139 - 298	28 - 60
Advanced Treatment – MF/GAC	131 - 280	50 - 108	181 - 388	36 - 78
Incremental Increase to Advanced Treatment MF/RO	48 - 104	26 - 56	75 - 160	15 - 32
Incremental Increase to Advanced Treatment MF/GAC	71 - 153	45 - 97	117 - 250	23 - 50

* The additional cost to increase the SRT to upwards of 30-days is about $12 - 20 million additional dollars in total project cost for a 5 mgd design flow

** Assumes zero liquid discharge for RO brine management, followed by evaporation ponds. Other options are available as listed in Section 4.4.2.

O&M=operations and maintenance; MF/RO=membrane filtration/reverse osmosis; MF/GAC=membrane filtration/granulated activated carbon; gpd=gallons per day

4.7.4 Unit Cost Assessment

Costs presented above are based on a treatment capacity of 5.0 mgd, however, existing treatment facilities range dramatically across Washington in size and flow treated. Table 9 indicates that the unit capital cost for baseline conventional secondary treatment for 5.0 mgd ranges between $13 to 28 per gallon per day of treatment capacity. The unit cost for the advanced treatment alternatives increases the range from the low $20s to upper $70s on a per-gallon per-day of capacity. The increase in cost for the advanced treatment alternatives is discussed in the sub-sections below.

Advanced Treatment MF/RO

The advanced treatment MF/RO alternative has a total present worth unit cost range of $28 to $60 million in per gallon per day of capacity. This translates to an incremental cost increase with respect to the baseline of $15 to $32 million dollars in per gallon per day treatment capacity. The key differences in cost between the baseline and the advanced treatment MF/RO are as follows:

- Larger aeration basins than the baseline to account for the longer SRT (<8 days versus >8 days).
- Additional pumping stations to pass water through the membrane facilities (MF and RO). These are based on peak flows.
- Membrane facilities (MF and RO; equipment, tanks chemical feed facilities, pumping, etc.) and replacement membrane equipment.
- Additional energy and chemical demand to operate the membrane facilities (MF and RO) and GAC.
- Zero liquid discharge facilities to further concentrate the brine reject.
- Zero liquid discharge facilities are energy/chemically intensive and they require membrane replacement every few years due to the brine reject water quality.
- An evaporation pond to handle the brine reject that has undergone further concentration by zero liquid discharge.

The advanced treatment MF/RO assumes that 100 percent of the flow is treated by MF, followed by 50 percent of the flow treated with RO. Sending a portion of flow through the RO and blending it with the balance of plant flows ensures a stable water to discharge. The RO brine reject (about 1.0 mgd) undergoes ZLD pre-treatment that further concentrates the brine reject to about 0.1-0.5 mgd. The recovery for both RO and ZLD processes is highly dependent on water quality (e.g., silicate levels).

ZLD technologies are effective at concentrating brine reject, but it comes at a substantial cost ($17.5 per gallon per day of ZLD treatment capacity of brine reject). The zero liquid discharge estimate was similar in approach to the demonstration study by Burbano and Brandhuber (2012) for La Junta, Colorado. The ability to further concentrate brine reject was critical from a management standpoint. Although 8 different options were presented for managing brine reject in Section 4.4.2, none of them is an attractive approach for handling brine reject. ZLD provides a viable pre-treatment step that requires subsequent downstream treatment. Evaporation ponds following ZLD were used for this study. Without ZLD, the footprint would be 3-5 times greater.

Roughly 30 acres of evaporation ponds, or more, may be required to handle the ZLD concentrate, depending upon concentrator effectiveness, local climate conditions, residuals

accumulation, residual removal, etc. Precipitation throughout Washington is highly variable which can greatly influence evaporation pond footprint. The approach for costing the evaporation pond was in accordance with Mickley et al. (2006) and the cost was about $2.6 million.

Recent discussions with an industry installing evaporation ponds revealed that they will use mechanical evaporators to enhance evaporation rates. The use of mechanical evaporators was not included in this study, but merits consideration if a facility is performing a preliminary design that involves evaporation ponds. The mechanical evaporators have both a capital costs and annual energy costs.

Advanced Treatment MF/GAC

The advanced treatment MF/GAC alternative has a total present worth unit cost range of $36 to $78 million in per gallon per day capacity. This translates to an incremental cost increase with respect to the baseline of $23 to $50 million dollars on a per gallon per day of treatment capacity basis. The key differences in cost between the baseline and the advanced treatment MF/GAC are as follows:

- Larger aeration basins than the baseline to account for the longer SRT (<8 days versus >8 days).
- Additional pumping stations to pass water through the MF membrane and GAC facilities. These are based on peak flows.
- GAC facilities (equipment, contact tanks, pumping, GAC media, etc.)
- Additional energy to feed and backwash the GAC facilities.
- GAC media replacement was the largest contributor of any of the costs.
- Additional hauling and fees to regenerate GAC off-site.

The advanced treatment MF/GAC assumes that 100 percent of the flow is treated by MF, followed by 100 percent of the flow treated with GAC. The GAC technology is an established technology. The costing approach was in accordance with EPA guidelines developed in 1998.

The critical issue while costing the GAC technology is whether a GAC vendor/regeneration facility is located within the region. On-site regeneration is an established technology with a furnace.

However, there are several concerns as listed in Section 4.4.3:

- Ability to obtain an air emissions permit
- Additional equipment to operate and maintain
- Energy and air emissions to operate a furnace on-site
- Operational planning to ensure that furnace is operating 90-95 percent of the time. Otherwise, operations is constantly starting/stopping the furnace which is energy intensive and deleterious to equipment
- If not operated properly, the facility has the potential to create hazardous/toxic waste to be disposed

If located within a couple hundred miles, off-site regeneration is preferred. For this study, off-site regeneration was assumed with a 250-mile (one-way) distance to the nearest vendor that can provide virgin GAC and a regeneration facility.

Incremental Treatment Cost

The difference in costs between the baseline and the advanced treatment alternatives is listed in Table 10. The incremental cost to retrofit the baseline facility to the advanced treatment was calculated by taking the difference between the two alternatives. These values should serve as a planning level benchmark for understanding the potential cost for retrofitting a particular facility. The incremental cost is unique to a particular facility. Several reasons for the wide range in cost in retrofitting a baseline facility to advanced treatment are summarized as follows:

- Physical plant site constraints. A particular treatment technology may or may not fit within the constrained particular plant site. A more expensive technology solution that is more compact may be required. Alternately, land acquisition may be necessary to enlarge a plant site to allow the addition of advanced treatment facilities. An example of the former is stacking treatment processes vertically to account for footprint constraints. This is an additional financial burden that would not be captured in the incremental costs presented in Table 10.
- Yard piping. Site specific conditions may prevent the most efficient layout and piping arrangement for an individual facility. This could lead to additional piping and pumping to convey the wastewater through the plant. This is an additional financial burden that would not be captured in the incremental costs presented in Table 10.
- Pumping stations. Each facility has unique hydraulic challenges that might require additional pumping stations not captured in this planning level analysis. This is an additional financial burden that would not be captured in the incremental costs presented in Table 10.

A cursory unit cost assessment was completed to evaluate how costs would compare for facilities with lower (0.5 mgd) and higher capacity (25 mgd), as presented in Table 10. Capital costs were also evaluated for a 0.5 mgd and 25 mgd facility using non-linear scaling equations with scaling exponents. The unit capital cost for baseline conventional secondary treatment for 0.5 mgd and 25 mgd is approximately $44 and $10 per gallon per day of treatment capacity, respectively. The incremental unit costs to implement an advanced treatment retrofit for 0.5 mgd would range between $30 to $96 per gallon per day of treatment capacity and would be site and discharger specific. The incremental unit costs to implement an advanced treatment retrofit for 25 mgd would range between $10 to 35 per gallon per day of treatment capacity and would be site and discharger specific. The larger flow, 25 mgd, is not as expensive on a per gallon per day of treatment capacity. This discrepancy for the 0.5 and 25 mgd cost per gallon per day of treatment capacity is attributed to economies of scale. Cost curve comparisons (potential total construction cost and total net present value) for the baseline and the two tertiary treatment options (MF/RO and MF/GAC) are shown in Figure 8 and Figure 9 between the flows of 0.5 and 25 mgd. It is important to note that while the economies of scale suggest lower incremental costs for the larger size facilities, some aspects of the advanced treatment processes may become infeasible at larger capacities due to factors such as physical space limitations and the large size requirements for components such as RO reject brine management.

Table 10. Treatment Technology Total Project Costs in 2013 Dollars for a 0.5 mgd Facility and a 25 mgd Facility

Alternative	Total Construction Cost, 2013 dollars ($ Million)	O&M Net Present Value, 2013 dollars ($ Million)*	Total Net Present Value, 2013 dollars ($ Million)	NPV Unit Cost, 2013 dollars ($/gpd)
0.5 mgd:				
Baseline (Conventional Secondary Treatment)	15 - 32	0.5 - 1.1	15 - 33	31 - 66
Advanced Treatment – MF/RO**	27 - 58	3.2 - 6.8	30 - 65	60 - 130
Advanced Treatment – MF/GAC	33 - 70	5 - 10.8	38 - 81	76 - 162
Incremental Increase to Advanced Treatment MF/RO	12 - 26	2.7 - 5.7	15 - 32	30 - 64
Incremental Increase to Advanced Treatment MF/GAC	18 - 38	4.6 - 9.8	22 - 48	45 - 96
25 mgd:				
Baseline (Conventional Secondary Treatment)	156 - 335	25 - 54	182 - 389	7 - 16
Advanced Treatment – MF/RO**	283 - 606	157 - 336	440 - 942	18 - 38
Advanced Treatment – MF/GAC	343 - 735	252 - 541	595 - 1276	24 - 51
Incremental Increase to Advanced Treatment MF/RO	127 - 272	131 - 281	258 - 553	10 - 22
Incremental Increase to Advanced Treatment MF/GAC	187 - 401	226.9 - 486	414 - 887	17 - 35

* Does not include the cost for labor.
** Assumes zero liquid discharge for RO brine management, followed by evaporation ponds. Other options are available as listed in Section 4.4.2.
MF/RO=membrane filtration/reverse osmosis
MF/GAC=membrane filtration/granulated activated carbon
O&M=operations and maintenance
gpd=gallons per day

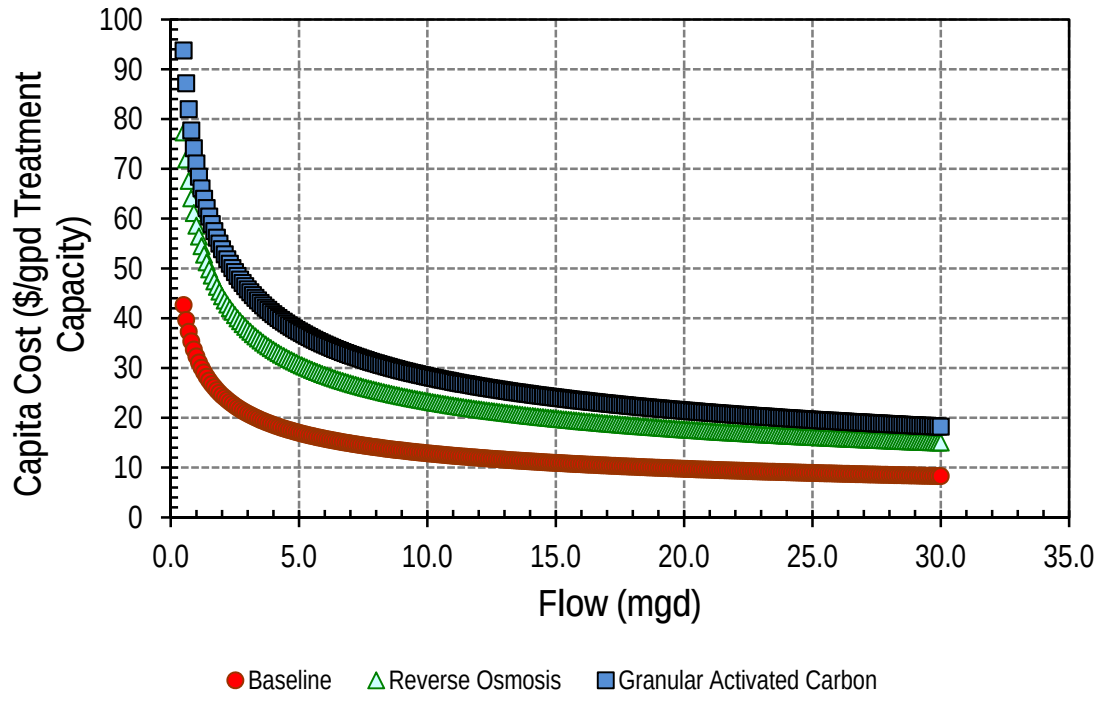

Figure 8: Capital Cost Curve Comparison for Baseline Treatment, MF/RO, and MF/GAC

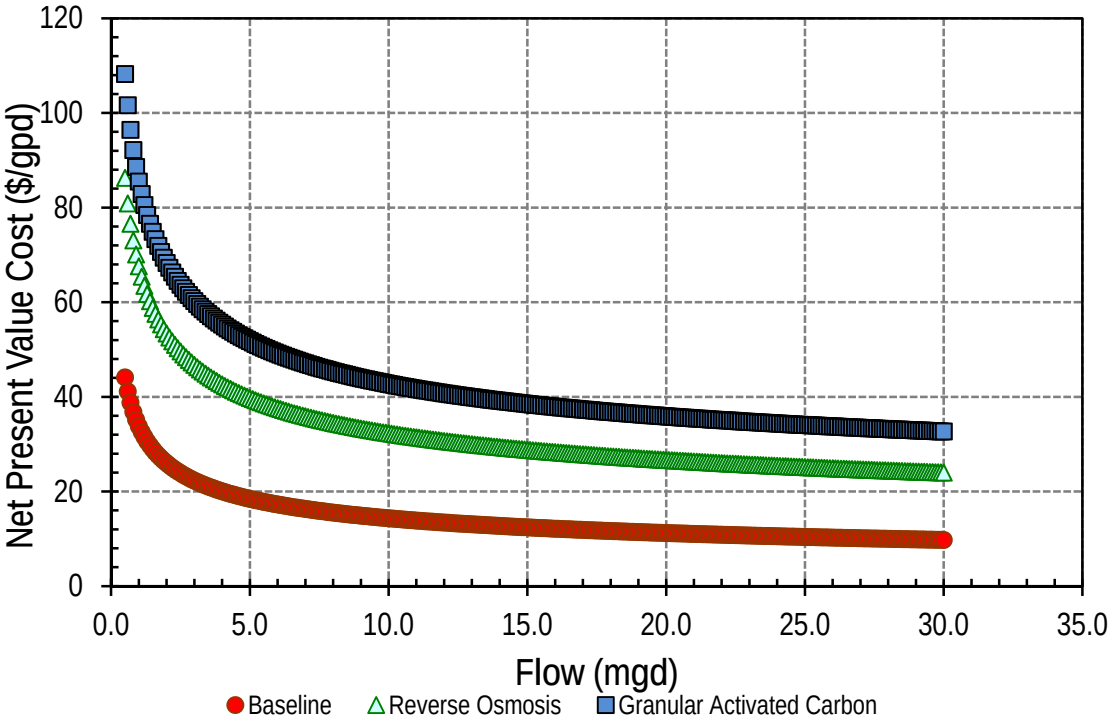

Figure 9: NPV Cost Curve Comparison for Baseline Treatment, MF/RO, and MF/GAC

4.8 Pollutant Mass Removal

An estimate of the projected load removal for the four constituents of concern was developed and is presented in Table 11. The current secondary effluent and advanced treatment effluent data is based on the only available data to HDR and is from municipal treatment plant facilities. Data is not available for advanced treatment facilities such as MF/RO or MF/GAC. Due to this lack of data, advanced treatment using MF/RO or MF/GAC was assumed to remove an additional zero to 90 percent of the constituents presented resulting in the range presented in Table 11. It is critical to note these estimates are based on limited data and are presented here simply for calculating mass removals. Current secondary effluent for industrial facilities would likely be greater than the data presented here and as a result, the projected effluent quality for industrial facilities would likely be higher as well. Based on the limited actual data from municipal treatment facilities, Table 11 indicates that mercury and BAP effluent limits may potentially be met using advanced treatment at facilities with similar existing secondary effluent quality.

Table 11. Pollutant Mass Removal by Contaminant for a 5 mgd Facility

Component	PCBs	Mercury	Arsenic	BAP
Required HHWQC based Effluent Quality (µg/L)	0.0000064	0.005	0.018	0.0013
Current Secondary Effluent Concentration (µg/L)*	0.0015	0.025	7.5	0.00031
Projected Effluent Quality (µg/L) from Advanced Treatment (MF/RO or MF/GAC)*	0.000041 – 0.00041	0.00012 – 0.0012	0.38 – 3.8	0.000029 - 0.00029
Mass Removed (mg/d)**	21 - 28	451 - 471	71,000 – 135,000	0.4 – 5.0
Mass Removed (lb/d)**	0.000045 – 0.000061	0.00099 – 0.0010	0.16 – 0.30	0.0000010 – 0.0000012

* Based on or estimated for actual treatment plant data from municipal facilities. Data sets are limited and current secondary effluent for industrial facilities would likely be greater than the data presented here.
** 1 lb = 454,000 mg
HHWQC=human health-based water quality criteria
MF/RO=membrane filtration/reverse osmosis
MF/GAC=membrane filtration/granulated activated carbon
µg/L=micrograms per liter
mg/d=milligrams per day
lb/d=pounds per day

Unit costs were developed based on required mass removal from a 5 mgd facility for each of the four constituents of concern to reduce discharges from current secondary effluent quality to the assumed required effluent quality (HHWQC). It important to note that this study concludes it is unclear if existing technology can meet the required effluent quality, however, the information presented in Table 12 assumes HHWQC would be met for developing unit costs. The unit costs are expressed as dollars in NPV (over a 25 year period) per pound of constituent removed over the same 25 year period using advanced treatment with MF/RO. The current secondary effluent quality data presented are based on typical secondary effluent quality expected for a municipal/industrial discharger. Table 12 suggests unit costs are most significant in meeting the PCB, mercury, and PAH required effluent quality.

Table 12. Unit Cost by Contaminant for a 5 mgd Facility Implementing Advanced Treatment using MF/RO

Component	PCBs	Mercury	Arsenic	PAHs
Required HHWQC based Effluent Quality (µg/L)	0.0000064	0.005	0.018	0.0013
Current Secondary Effluent Concentration (µg/L)*	0.002	0.025	7.5	0.006
Total Mass Removed (lbs) over 25-year Period	0.76	7.6	2,800	1.8
Unit Cost (NPV per total mass removed in pounds over 25 years)	$290,000,000	$29,000,000	$77,000	$120,000,000

*Derived from data presented in Table 3.
**Based on assumed 25-year NPV of $219,000,000 (average of the range presented in Table 10) and advanced treatment using MF/RO.
NPV=net present value
HHWQC=human health-based water quality criteria
µg/l=micrograms per liter

4.9 Sensitivity Analysis

The ability of dischargers to meet a HHWQC one order of magnitude less stringent (than HHWQC presented in Table 3 and used in this report) was considered. The same advanced treatment technologies using MF/RO or MF/GAC would still be applied to meet revised effluent quality one order-of-magnitude less stringent despite still not being able to meet less stringent effluent limits. As a result, this less stringent effluent quality would not impact costs. Based on available data, it appears the mercury and BAP limits would be met at a less stringent HHWQC. PCB effluent quality could potentially be met if advanced treatment with RO or GAC performed at the upper range of their projected treatment efficiency. It does not appear the less stringent arsenic HHWQC would be met with advanced treatment. It is important to note that a discharger's ability to meet these less stringent limits depends on existing secondary effluent characteristics and is facility specific. Facilities with higher secondary effluent constituent concentrations will have greater difficulty meeting HHWQC.

5.0 Summary and Conclusions

This study evaluated treatment technologies potentially capable of meeting revised effluent discharge limits associated with revised HHWQC. HDR completed a literature review of potential technologies and engineering review of their capabilities to evaluate and screen treatment methods for meeting revised effluent limits for four constituents of concern: arsenic, BAP, mercury, and PCBs. HDR selected two alternatives to compare against a baseline, including enhanced secondary treatment, enhanced secondary treatment with MF/RO, and enhanced secondary treatment with MF/GAC. HDR developed capital costs, operating costs, and a NPV for each alternative, including the incremental cost to implement from an existing secondary treatment facility.

The following conclusions can be made from this study.

- Revised HHWQC based on state of Oregon HHWQC (2001) and EPA "National Recommended Water Quality Criteria" will result in very low water quality criteria for toxic constituents.
- There are limited "proven" technologies available for dischargers to meet required effluent quality limits that would be derived from revised HHWQC.
    - Current secondary wastewater treatment facilities provide high degrees of removal for toxic constituents; however, they will not be capable of compliance with water quality-based NPDES permit effluent limits derived from revised HHWQC.
    - Advanced treatment technologies have been investigated and candidate process trains have been conceptualized for toxics removal.
        - Advanced wastewater treatment technologies may enhance toxics removal rates, however they will not be capable of compliance with HHWQC based effluent limits for PCBs. The lowest levels achieved based on the literature review were between <0.00001 and 0.00004 µg/L, as compared to a HHWQC of 0.0000064 µg/L.
        - Based on very limited performance data for arsenic and mercury from advanced treatment information available in the technical literature, compliance with revised criteria may or may not be possible, depending upon site specific circumstances.
            - Compliance with a HHWQC for arsenic of 0.018 µg/L appears unlikely. Most treatment technology performance information available in the literature is based on drinking water treatment applications targeting a much higher SDWA MCL of 10 µg/L.
            - Compliance with a HHWQC for mercury of 0.005 µg/L appears to be potentially attainable on an average basis but perhaps not if effluent limits are structured on a maximum monthly, weekly or daily basis. Some secondary treatment facilities attain average effluent mercury levels of 0.009 to 0.066 µg/L. Some treatment facilities with effluent filters attain average effluent mercury levels of 0.002 to 0.010 µg/L. Additional advanced treatment processes are expected to enhance these removal rates, but little mercury performance data is available for a definitive assessment.
        - Little information is available to assess the potential for advanced technologies to comply with revised benzo(a)pyrene criteria. A municipal wastewater treatment plant study reported both influent and effluent BAP concentrations less than the HHWQC of 0.0013 ug/L (Ecology, 2010).

  - Some technologies may be effective at treating identified constituents of concern to meet revised limits while others may not. It is therefore even more challenging to identify a technology that can meet all constituent limits simultaneously.
  - A HHWQC that is one order-of-magnitude less stringent could likely be met for mercury and PAHs however it appears PCB and arsenic limits would not be met.
- Advanced treatment processes incur significant capital and operating costs.
  - Advanced treatment process to remove additional arsenic, benzo(a)pyrene, mercury, and PCBs would combine enhancements to secondary treatment with microfiltration membranes, reverse osmosis, and granular activated carbon and increase the estimated capital cost of treatment from $17 to $29 in dollars per gallon per day of capacity (based on a 5.0 mgd facility).
  - The annual operation and maintenance costs for the advanced treatment process train will be substantially higher (approximately $5 million - $15 million increase for a 5.0 mgd capacity facility) than the current secondary treatment level.
- Implementation of additional treatment will result in additional collateral impacts.
  - High energy consumption.
  - Increased greenhouse gas emissions.
  - Increase in solids production from chemical addition to the primaries. Additionally, the membrane and GAC facilities will capture more solids that require handling.
  - Increased physical space requirements at treatment plant sites for advanced treatment facilities and residuals management including reverse osmosis reject brine processing.
- It appears advanced treatment technology alone cannot meet all revised water quality limits and implementation tools are necessary for discharger compliance.
  - Implementation flexibility will be necessary to reconcile the difference between the capabilities of treatment processes and the potential for HHWQC driven water quality based effluent limits to be lower than attainable with technology

6.0 References

Ahn, J.-H., Kim, S, Park, H., Rahm, B., Pagilla, K., Chandran, K. 2010. N2O emissions from activated sludge processes, 2008-2009: Results of a national surveying program in the United States. Environ. Sci. Technol., 44(12):4505-4511.

Andrianisa, H.,A., Ito, A., Sasaki, A., Aizawa, J., and Umita, T. 2008. Biotransformation of arsenic species by activated sludge and removal of bio-oxidised arsenate from wastewater by coagulation with ferric chloride. Water Research, 42(19), pp. 4809-4817

Andrianisa, H.,A., Ito, A., Sasaki, A., Ikeda, M., Aizawa, J., and Umita, T. 2006. Behaviour of arsenic species in batch activated sludge process: biotransformation and removal. Water Science and Technology, 54(8), pp. 121-128.

Burbano, A and Brandhuber, P. (2012) Demonstration of membrane zero liquid discharge for drinking water systems. Water Environment Research Federation (WERF) Report WERF5T10.

California Air Resources Board, ICLEI, California Climate Action Registry, The Climate Registry. 2008. Local Government Operations Protocol. For the quantification and reporting of greenhouse gas emissions inventories, Version 1.1.

Chung, B., Cho, J., Song, C., and Park, B. Degradation of naturally contaminated polycyclic aromatic hydrocarbons in municipal sewage sludge by electron beam irradiation. Bulletin of Environmental Contamination and Toxicology, 81(1), pp. 7-11.

CRITFC (Columbia River Inter-Tribal Fish Commission). 1994. A fish consumption survey of the Umatilla, Nez Perce, Yakama and Warm Springs Tribes of the Columbia River Basin. Columbia River Inter-Tribal Fish Commission Report reference #94-03, Portland, Oregon.

Eckenfelder, W.W., Industrial Water Pollution Control, 2nd ed. (New York: McGraw-Hill, 1989).

Ecology. 2010. (Lubliner, B., M. Redding, and D. Ragsdale). Pharmaceuticals and Personal Care Products in Municipal Wastewater and Their Removal by Nutrient Treatment Technologies. Washington State Department of Ecology, Olympia, WA. Publication Number 10-03-004.

González, D., Ruiz, L.M., Garralón, G., Plaza, F., Arévalo, J., Parada, J., Péreza, J., Morenoa, B., and Ángel Gómez, M. 2012. Wastewater polycyclic aromatic hydrocarbons removal by membrane bioreactor. Desalination and Water Treatment, 42, pp. 94–99

Grosser, J. 2010. The Challenge: Measure Arsenic in Drinking Water. White paper.

Haapeaa, P., and Tuhkanen, T. 2006. Integrated treatment of PAH contaminated soil by soil washing, ozonation and biological treatment . Journal of Hazardous Materials,136(21), pp. 244–250

Intergovernmental Panel on Climate Change. 2006. 2006 IPCC Guidelines for National Greenhouse Gas Inventories. Prepared by the National Greenhouse Gas Inventories Programme, Eggleston, S., Buendia, L., Miwa, K., Ngara, T., Tanabe, K. (eds.) Published: IGES, Japan.

LaGrega, M.D., Buckingham P.L. and Evans J.C., Hazardous Waste Management, 1st ed. (New York: McGraw-Hill, 1994).

Melcer, H., Steel, P., and Bedford, W.K. 1993. Removal of polycyclic aromatic hydrocarbons and hetercyclic nitrogenous compounds by a POTW receiving industrial discharges. Proceeding of WEFTEC 1993.

Mickley and Associates. 2006. Membrane Concentrate Disposal: Practices and Regulations. U.S. Department of the Interior, Bureau of Reclamation, Contract No. 98-FC-81-0054.

National Council for Air and Stream Improvement, Inc. (NCASI). 1998. Technical and economic feasibility assessment of metals reduction in pulp and paper mill wastewaters. Technical Bulletin No. 756. Research Triangle Park, NC: National Council for Air and Stream Improvement, Inc., 1998.

National Council for Air and Stream Improvement, Inc. (NCASI). 2004. Investigation of advanced techniques to remove low-level mercury from pulp and paper mill effluents. Technical Bulletin No. 870. Research Triangle Park, NC: National Council for Air and Stream Improvement, Inc.

National Council for Air and Stream Improvement, Inc. (NCASI). 2000. Memorandum: Information on PCB Water Quality Criteria, Analytical Methods, and Measurement Results for Point Sources and Ambient Waters. Technical Bulletin No. 807. Research Triangle Park, NC: National Council for Air and Stream Improvement, Inc.

National Council for Air and Stream Improvement, Inc. (NCASI). 2000. Bench scale testing of processes to reduce metals concentrations in pulp and paper mill wastewaters. Technical Bulletin No. 807. Research Triangle Park, NC: National Council for Air and Stream Improvement, Inc.

Ning, R. 2002. Arsenic removal by reverse osmosis. Desalination, 143 (3), pp. 237–241

Oleszczuk, P., Hale, S. E., Lehmann, J., and Cornelissen, G. 2012. Activated carbon and biochar amendments decrease pore-water concentrations of polycyclic aromatic hydrocarbons (PAHs) in sewage sludge. Bioresource Technology, 111, pp. 84–91

Oregon Department of Environmental Quality. 2011. Table 40: Human Health Water Quality Criteria for Toxic Pollutants, Effective October 17, 2011. Available on-line at: http://www.deq.state.or.us/wq/standards/toxics.htm

Owen, W.F. 1982. Energy in Wastewater Treatment. Prentice-Hall, Englewood Cliffs, New Jersey.

Parker, W., Monteith, H., and Pileggi, V. 2009. Estimation of Biodegradation and Liquid-Solid Partitioning Coefficients for Complex PAHs in Wastewater Treatment. Proceedings of the Water Environment Federation 2009, pp. 2537-2554.

Rodrigue, P., and Rielly, A. 2009. Effectiveness of a membrane bioreactor on weak domestic wastewater containing polychlorinated biphenyls. Proceedings of the Water Environment Federation, Microconstituents and Industrial Water Quality 2009, pp. 174-184(11)

Russo, L., Rizzo, L., and Belgiorno, V. 2012. Ozone oxidation and aerobic biodegradation with spent mushroom compost for detoxification and benzo(a)pyrene removal from contaminated soil. Chemosphere, 87(6), pp. 595-601

SimaPro 6. 2008. Life Cycle Analysis Software. The Netherlands.

Sponza, D., and Oztekin, R. 2010. Effect of sonication assisted by titanium dioxide and ferrous ions on polyaromatic hydrocarbons (PAHs) and toxicity removals from a petrochemical industry wastewater in Turkey. Journal of Chemical Technology & Biotechnology, 85(7), pp. 913-925

U.S. Environmental Protection Agency (EPA). 2003. Arsenic Treatment Technology Handbook for Small Systems, EPA 816R03014.

U.S. Environmental Protection Agency. 2000. Methodology for Deriving Ambient Water Quality Criteria for the Protection of Human Health. EPA- 822-B-00-004, October 2000.

U.S. Environmental Protection Agency. 2007. The Emissions & Generation Resource Integrated Database – eGrid WebVersion1.0. United States Environmental Protection Agency, Washington, D.C.

U.S. Department of Agriculture (USDA). 1998. Continuing survey of food intakes by individuals: 1994-96, 1998. U.S. Department of Agriculture, Agricultural Research Service.

Water Environment Federation. 2009. Design of Municipal Wastewater Treatment Plants, WEF Manual of Practice 8, Fourth Edition, ASCE Manuals and Reports on Engineering Practice No. 76, Volume 1. Alexandria, VA.

Water Environment Research Foundation (WERF). 2012. Demonstration of Membrane Zero Liquid Discharge for Drinking Water Systems, A Literature Review. WERF5T10.

Water Environment Research Foundation (WERF). 2011. Striking the Balance Between Nutrient Removal in Wastewater Treatment and Sustainability. NUTR1R06n.

WesTech brochure. Victorville case study. Vendor Brochure.

Williams, M. 2003. A Review of Wastewater Treatment by Reverse Osmosis. White paper

Yerushalmi, L., Nefil, S., Hausler, R., and Guiot, S. 2006. Removal of pyrene and benzo(a)pyrene from contaminated water by sequential and simultaneous ozonation and biotreatment. Water Environment Research, 78 (11).

Zeng, Y., Hong, A., and Wavrek, D. 2000. Integrated chemical-biological treatment of benzo[a]pyrene. Environmental Science and Technology, 34 (5), pp 854–862

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7.0 Appendices

- Appendix A - Unit Process Sizing Criteria
- Appendix B - Greenhouse Gas Emissions Calculation Assumptions

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APPENDIX A - UNIT PROCESS SIZING CRITERIA

Table A-1. Unit Processes Sizing Criteria for Each Alternative

Unit Process	Units	Baseline Treatment	Advanced Treatment	Comment
Influent Pumping Station	unitless	3 Times Ave Flow	3 Times Ave Flow	This is peaking factor used to size the pumps (peak flow:average flow)
Alum Dose for CEPT (optional)	mg/L	20	20	This is the metal salt upstream of the primaries
Primary Clarifiers	gpd/sf	1000	1000	This is for average annual flows
Primary Solids Pumping Station	unitless	1.25 Times Ave Flow	1.25 Times Ave Flow	This is peaking factor used to size the pumps (maximum month flow:average flow)
Aeration System Oxygen Uptake Rate (OUR)	mg/L/hr	25	25	Average annual OUR is used in tandem with mixed liquor to determine the required aeration basin volume (the limiting parameter governs the activated sludge basin volume)
Aeration Basin Mixed Liquor	mg/L	1250	2500	Average annual mixed liquor is used in tandem with OUR (see next row) to determine the required aeration basin volume (the limiting parameter governs the activated sludge basin volume)
Secondary Clarifiers Hydraulic Loading	gpd/sf	650	--	Only use for Baseline as clarifiers governed hydraulically with short SRT (<2 days)
Secondary Clarifiers Solids Loading	lb/d/sf	--	24	Only use for Advanced Treatment as clarifiers governed by solids with long SRT (>8 days)
Return Activated Sludge (RAS) Pumping Station	unitless	1.25 Times Ave Flow	1.25 Times Ave Flow	RAS must have capacity to meet 100% influent max month Flow. The influent flow is multiplied by this peaking factor to determine RAS pumping station capacity.
Waste Activated Sludge (WAS) Pumping Station	gpm	1.25 Times Ave Flow	1.25 Times Ave Flow	WAS must have capacity to meet max month WAS flows. The average annual WAS flow is multiplied by this peaking factor to determine WAS pumping station capacity.
Microfiltration (MF) Flux	gfd	--	25	Based on average annual pilot experience in Coeur D'Alene, ID
MF Backwash Storage Tank	unitless	--	1.25	Storage tanks must have capacity to meet maximum month MF backwash flows. The average annual MF backwash volume is multiplied by this peaking factor to determine required volume.

Table A-1. Unit Processes Sizing Criteria for Each Alternative

Unit Process	Units	Baseline Treatment	Advanced Treatment	Comment
MF Backwash Pumps	unitless	--	1.25	Backwash pumps must have capacity to meet maximum month MF backwash flows. The average annual MF backwash flow is multiplied by this peaking factor to determine required flows.
Reverse Osmosis (RO)	gallon per square foot per day (gfd)	--	10	
RO Reject	%	--	20	This represents the percentage of feed flow that is rejected as brine
Chlorination Dose	mg/L	15	15	
Chlorination Storage Capacity	days	14	14	
Chlorine Contact Tank	min	30	30	This is for average annual conditions.
Dechlorination Dose	mg/L	15	15	
Dechlorination Storage Capacity	days	14	14	
Gravity Belt Thickener	gpm/m	200	200	This is for maximum month conditions using the 1.25 peaking factor from average annual to maximum month
Anaerobic Digestion	Hydraulic residence time (HRT)	18	18	This is for average annual conditions
Dewatering Centrifuge	gpm	120	120	This is for maximum month conditions using the 1.25 peaking factor from average annual to maximum month

gpd=gallons per day; sf=square feet; gpm=gallons per minute

Appendix B – Greenhouse Gas Emissions Calculation Assumptions

The steady state mass balance results were used to calculate GHG emissions. The assumptions used to convert between energy demand, chemical demand and production, as well as biologically-mediated gases (i.e., CH4 and N2O) and GHG emissions are provided in Table B-1. The assumptions are based on EPA (2007) values for energy production, an adaptation of the database provided in Ahn et al. (2010) for N2O emissions contribution, Intergovernmental Panel on Climate Change (IPCC) (2006) for fugitive CH4 emissions, and various resources for chemical production and hauling from production to the wastewater treatment plant (WWTP). Additionally, the biogas produced during anaerobic digestion that is used as a fuel source is converted to energy with MOP8 (2009) recommended waste-to-energy values.

Table B-1. Greenhouse Gas Emissions Assumptions

Parameters	Units	Value	Source
N_2O to CO_2 Conversion	lb CO_2/lb N_2O	296	IPCC, 2006
CH_4 to CO_2 Conversion	lb CO_2/lb CH_4	23	IPCC, 2006
Energy Production			
CO_2	lb CO_2/MWh	1,329	USEPA (2007)
N_2O	lb N_2O/GWh	20.6	USEPA (2007)
CH_4	lb CO_2/GWh	27.3	USEPA (2007)
Sum Energy Production	lb CO_2/MWh	1336	USEPA (2007)
GHGs per BTU Natural Gas			
CO_2	lb CO_2/MMBTU Natural Gas	52.9	CA Climate Action Registry Reporting Tool
N_2O	lb N_2O/MMBTU Natural Gas	0.0001	CA Climate Action Registry Reporting Tool
CH_4	lb CO_2/MMBTU Natural Gas	0.0059	CA Climate Action Registry Reporting Tool
Sum Natural Gas		53.1	CA Climate Action Registry Reporting Tool
Non-BNR N_2O Emissions	g N_2O/PE/yr	32	Ahn et al. (2010)
BNR N_2O Emissions	g N_2O/PE/yr	30	Ahn et al. (2010)
Biogas Purity	% Methane	65	WEF, 2009
Biogas to Energy	BTU/cf CH4	550	WEF, 2009
Digester Gas to Electrical Energy Transfer Efficiency	%	32	HDR Data

Table B-1. Greenhouse Gas Emissions Assumptions

Parameters	Units	Value	Source
Chemical Production			
Alum	lb CO_2/lb Alum	0.28	SimaPro 6.0 - BUWAL250, Eco-indicator 95
Polymer	lb CO_2/lb Polymer	1.18	Owen (1982)
Sodium Hypochlorite	lb CO_2/lb Sodium Hypochlorite	1.07	Owen (1982)
Building Energy Efficiency	kBTU/sf/yr	60	Calif. Commercial End-Use Survey (2006)
Hauling Distance		-	
Local	miles	100	-
Hauling Emissions			
Fuel Efficiency	miles per gallon	8	
CO_2	kg CO_2/gal diesel	10.2	CA Climate Action Registry Reporting Tool
N_2O	kg N_2O/gal diesel	0.0001	CA Climate Action Registry Reporting Tool
CH_4	kg CH_4/gal diesel	0.003	CA Climate Action Registry Reporting Tool
Sum Hauling Fuel	kg CO_2/gal diesel	10.2	CA Climate Action Registry Reporting Tool

GWh = Giga Watt Hours
MWh = Mega Watt Hours
MMBTU = Million British Thermal Units
BTU = British Thermal Unit
PE = Population Equivalents
kBTU/sf/yr = 1,000 British Thermal Units per Square Foot per Year
cf = cubic feet
lb = pound
kg = kilogram
gal = gallon

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Epidemiologic confirmation that fruit consumption influences mercury exposure in riparian communities in the Brazilian Amazon

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Abstract

Since deforestation has recently been associated with increased mercury load in the Amazon, the problem of mercury exposure is now much more widespread than initially thought. A previous exploratory study suggested that fruit consumption may reduce mercury exposure. The objectives of the study were to determine the effects of fruit consumption on the relation between fish consumption and bioindicators of mercury (Hg) exposure in Amazonian fish-eating communities. A cross-sectional dietary survey based on a 7-day recall of fish and fruit consumption frequency was conducted within 13 riparian communities from the Tapajós River, Brazilian Amazon. Hair samples were collected from 449 persons, and blood samples were collected from a subset of 225, for total and inorganic mercury determination by atomic absorption spectrometry. On average, participants consumed 6.6 fish meals/week and ate 11 fruits/week. The average blood Hg (BHg) was 57.1 ± 36.3 μg/L (median: 55.1 μg/L), and the average hair-Hg (HHg) was 16.8 ± 10.3 μg/g (median: 15.7 μg/g). There was a positive relation between fish consumption and BHg ($r = 0.48$; $P < 0.0001$), as well as HHg ($r = 0.34$; $P < 0.0001$). Both fish and fruit consumption entered significantly in multivariate models explaining BHg (fish: $\beta = 5.6$, $P < 0.0001$; fruit: $\beta = -0.5$, $P = 0.0011$; adjusted model $R^2 = 36.0\%$) and HHg levels (fish: $\beta = 1.2$, $P < 0.0001$; fruit: $\beta = -0.2$, $P = 0.0002$; adjusted model $R^2 = 21.0\%$). ANCOVA models showed that for the same number of fish meals, persons consuming fruits more frequently had significantly lower blood and HHg concentrations. For low fruit consumers, each fish meal contributed 9.8 μg/L Hg increase in blood compared to only 3.3 μg/L Hg increase for the high fruit consumers. In conclusion, fruit consumption may provide a protective effect for Hg exposure in Amazonian riparians. Prevention strategies that seek to maintain fish consumption while reducing Hg exposure in fish-eating communities should be pursued.

Keywords: Fish consumption; Fruit consumption; Mercury exposure; Amazon; Brazil

1. Introduction

Over the last decades, the presence of mercury (Hg) in the Amazon and its potential human health risks has given rise to much concern. During the 1970s, intense gold-mining activities were undertaken, with the arrival of thousands of gold miners coming from other regions of Brazil (Cleary, 1990; Santos et al., 1992). Although elevated Hg levels found in the Amazonian environment were initially attributed to these gold-mining activities (Hylander, 1994; Malm et al., 1990; Nriagu et al., 1992), more recent studies have shown high Hg concentrations both in fish and human tissues in regions where there has been no gold-mining (Guimarães et al., 1999; Silva-Forsberg et al., 1999; Dórea et al., 2003). Indeed, Amazonian soils constitute important reservoirs of Hg

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(Roulet et al., 1998, 1999, 2000; Fadini and Jardim, 2001), and a significant part of Hg contamination of the aquatic ecosystems is caused by erosion of such soils following deforestation for agriculture and/or cattle (Almeida et al., 2005; Farella et al., 2001, 2006; Roulet et al., 1999). Thus in the Amazonian environment, Hg from different sources is available for methylation processes contaminating the fish resources, which constitute a dietary mainstay for the large population living along the riverbanks (Dolbec et al., 2001; Guimarães, 2001; Lebel et al., 1997). Epidemiologic studies of riparian populations have shown dose-related associations between fish consumption, methyl mercury (MeHg) exposure, and early adverse health effects. Deficits in neurological and neuropsychological functions, as well as cytogenetic changes have been reported among adults and/or children from this area (Amorim et al., 2000; Cordier et al., 2002; Dolbec et al., 2000; Grandjean et al., 1999; Harada et al., 2001; Lebel et al., 1998, 1996; Yokoo et al., 2003). Additionally, recent exploratory studies in the Tapajós region suggest that Hg exposure may be associated with both increased blood pressure (Fillion et al., 2006) and autoimmune dysfunction (Silva et al., 2004).

There is a large variation in Hg levels in fish from the Tapajós region. A recent report indicated Hg concentrations above the recommended value of 0.5 μg/g in 31% of predatory fish species (Silva et al., 2006). Another study presented high mean Hg levels for carnivorous species such as Dourada (*Brachyplatystoma flavicans*: 0.8 μg/g), Surubim (*Pseudoplatystoma* sp.: 0.8 μg/g), Pescada (*Plagisocion squamosissimus:* 0.6 μg/g), and Sarda (*Pelona* sp.: 0.7 μg/g), whereas low levels of Hg have been reported in herbivorous fish such as Aracu (*Leporinus* sp.: 0.07 μg/g), Pacu (*Mylossoma* sp.: 0.05 μg/g), and Tambaqui (*Colossoma macropomum*: 0.08 μg/g) (Santos et al., 2000). In the Tapajós region, fish appear to be the only food source for Hg. A recent study evaluating mercury pollution in cultivated and wild plant parts from the Tapajós region concluded that the translocation of Hg from soils throughout roots to aboveground is not significant (Egler et al., 2006). This is supported by European studies examining Hg levels in agricultural products of Hg-containing soils, which concluded that Hg intake through vegetables and fruits does not represent a health hazard for consumers (Ursinyová et al., 1997; Barghigiani and Ristori, 1994).

Since fish is a central and highly nutritious element in the Amazonian diet, some authors have minimized the importance of Hg exposure, suggesting that changes in fish consumption practices would necessarily have strong negative consequences for human health (Dórea, 2004; Dórea et al., 2005). An alternative public health approach would be to identify elements in the traditional diet that might influence Hg absorption and/or toxicity, thereby providing a way for this population to continue eating fish, while reducing Hg exposure. Despite the recognition that diet and nutrition can influence a population's vulnerability to the effects of MeHg (NRC, 2000), dietary information has not been systematically collected in most epidemiologic studies examining the effects of MeHg exposure (Chapman and Chan, 2000). Although a number of controlled experiments have estimated the effects of specific nutrients on Hg absorption and/or toxicity (Calabrese, 1978; Levander and Cheng, 1980; Imura and Naganuma, 1985; Whanger, 1992; Peraza et al., 1998; Lapina et al., 2000; Rao et al., 2001; Rao and Sharma, 2001; Usuki et al., 2001; Afonne et al., 2002), studies examining the role of diet in determining Hg concentrations in free-living populations are still scarce.

In a hypothesis-generating study of 26 adult women from a riparian village in the Brazilian Amazon, we examined the influence of the consumption of traditional foods on the relationship between fish consumption and Hg exposure (Passos et al., 2003). In that study, the women kept extensive food consumption frequency diaries, which included all food and beverages, for 12 months. The results of this food consumption survey revealed that the strong relationship between fish consumption and Hg exposure was significantly modified by fruit consumption.

The objective of the present study was to determine, in a large riparian population in the Brazilian Amazon, the effects of fruit consumption on the relation between fish consumption and bioindicators of Hg exposure, using an epidemiologic design. It is part of the CARUSO Project, a large interdisciplinary, ecosystemic study on Hg contamination and exposure in the region (CARUSO, 2007).

2. Methods

2.1. Study design and population

A cross-sectional dietary survey was undertaken among 13 riparian communities situated on the banks of the Tapajós River, a major tributary of the Amazon (Fig. 1). These communities were chosen in order to represent the diversity created throughout the colonization process, as some of them were established after colonization began in the early 1960s, whereas others were established up to 100 years before. Because of the difficulties in applying a random sampling strategy in this setting, a convenience sample was used. Age and sex distributions were then compared to the underlying population, which had previously been determined through a house-to-house survey, in each community (Table 1). During this survey, the study was explained at each household and persons were invited to participate. Additionally, community meetings were conducted in each village in order to further explain the study.

Approval was obtained from Ethics Committees of the Federal University of Rio de Janeiro (Brazil) and the University of Quebec in Montreal (Canada). The study was explained individually, and persons agreeing to participate signed an informed consent form that was read to them.

2.2. Assessment of fish and fruit consumption frequency

Because of important seasonal differences in the availability of fish species and types of fruit (Lebel et al., 1997; Dolbec et al., 2001; Passos et al., 2001), a 7-day dietary recall questionnaire (7-DDR) was used in order to determine recent fish and fruit consumption frequency. Development and validation studies of this instrument have shown that it is relatively easily administered and it constitutes a sensitive method to assess short-term food consumption (Hebert et al., 1997).

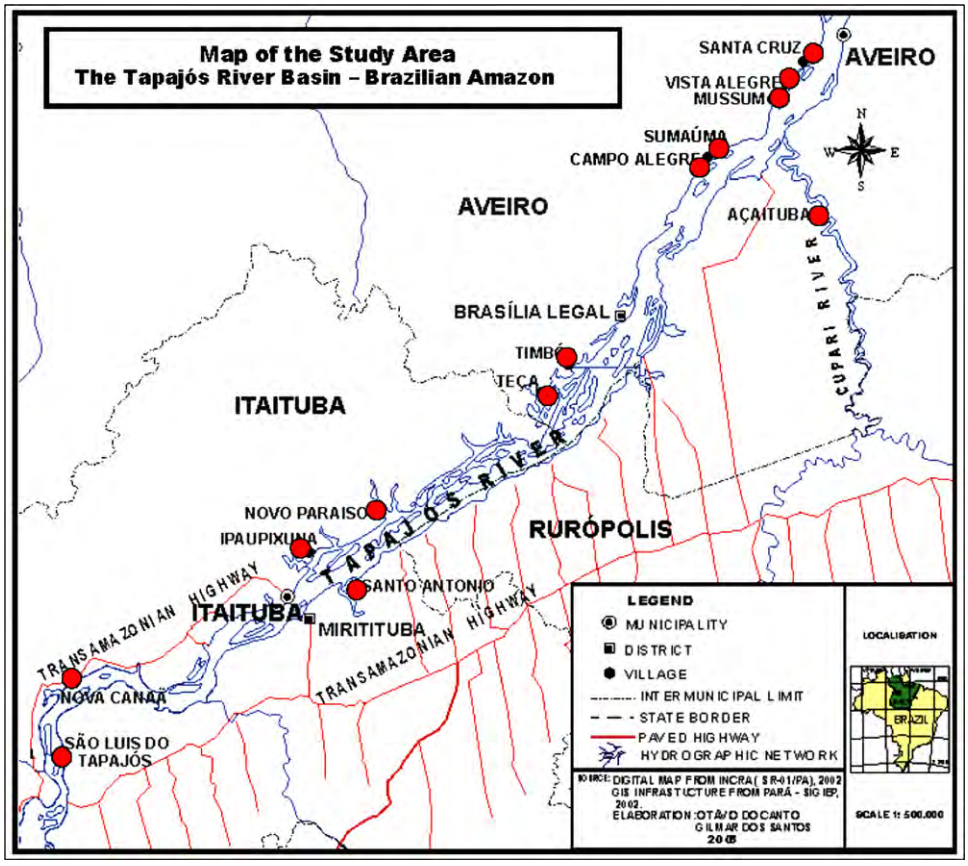

Fig. 1. Map of the study area. Participating communities are identified by a large red dot.

Table 1
Age distribution and rates of participation in the study population

Age category	Total adult population	Study population	% participation
15–24	427	112	26.2
25–34	260	102	39.2
35–44	218	97	44.5
45–54	161	54	33.5
55–64	116	50	43.1
⩾65	104	44	42.3
Total	1286	459	35.7

A list was prepared which included most of the fish and fruit species present in the region. In interviews performed over the months of June–August 2003, participants indicated the number of meals containing fish as well as the fish species that were consumed. As for fruits, the procedure was similar, but in this case, for each fruit species, the participant indicated the number of fruits that had been eaten each day over the preceding 7 days, whether during a meal or not. Fish and fruit species that were not in the initial list were also recorded.

2.3. Sampling and analyses of bioindicators

Hair samples were collected from 449 persons (211 men and 238 women) and blood samples were collected from a subset of 225 persons (114 men and 111 women). Hair strands from the occipital region were cut at the root and then placed in plastic bags, with the root end stapled. The samples were analyzed at the Laboratory of Radioisotopes of the Federal University of Rio de Janeiro (Brazil), by atomic absorption spectrometry with an AA 1475 Varian and a cold vapor generator accessory VGA-76 Varian. Mineralization of samples was done with mixtures of acids (HCl, HNO_3 and H_2SO_4) and oxidants ($KMnO_4$, $K_2S_20_7$ and H_2O_2), with techniques developed and adapted to the flow injection system vapor generator accessory (Malm et al., 1989). This laboratory participates regularly in inter-laboratory comparison programs for total and inorganic mercury analysis (Gill et al., 2002), and analytical quality control was ensured by the use of standard reference materials (Human Hair 085 and 086) provided by the International Atomic Energy Agency (IAEA).

Blood samples were collected by a nurse by venipuncture into 6 ml heparinized Becton Dickinson Vacutainer® (BD7863). All blood samples were kept frozen at −20° until analyzed. Total and inorganic mercury in blood were determined by atomic absorption spectrometry at the laboratory of the Quebec Toxicology Center of the Quebec Public Health Institute (CTQ-INSPQ), Canada, according to the method described by Ebbestadt et al. (1975). The detection limit for blood mercury (BHg) analysis was 0.2 μg/L and analytical quality control was ensured by the use of internal reference samples for blood analysis provided by the Inter-Laboratory Comparison Program conducted by the CTQ-INSPQ.

2.4. Statistical analysis

Descriptive statistics were used to describe the study population, Hg exposure as well as the results of fish and fruit consumption frequency. Correlation analyses were used to examine the relation between the frequency of consumption of specific fish species in relation to BHg and hair mercury (HHg) concentrations. Where appropriate, non-parametric techniques were used for comparisons.

The associations between fish and fruit consumption frequency with respect to BHg and HHg levels were assessed using simple and multiple linear regression models. BHg and HHg levels were the dependent variables in separate linear regression models, which tested for the influence of overall fish and fruit consumption; the latter were included as continuous independent variables.

All pregnant women were excluded from the analyses, and potential covariates such as alcohol consumption, gender, age, schooling, and cigarette smoking were included in the models. Analysis of covariance (ANCOVA) was used to test interactions. Results were defined as statistically significant for a value of $P \leqslant 0.05$. Analyses were performed using Statview for Windows Version 5.0.1 and JMP 5.0.1a (SAS Institute Inc.).

3. Results

Socio-demographic characteristics of the study population are shown in Table 2. Schooling varied between 0 and 12 years (mean 3.8 years $\pm$ 2.7), and the age range was 15–89 years (mean 38.6 years $\pm$ 17.2). Eighty-three percent (83%) of the participants were originally from the State of Pará, and 70% live on the Tapajós River banks, whereas 30% live on one of its tributaries. Fig. 2(A and B) presents the distribution of BHg and HHg levels, respectively. Overall, the average BHg was 57.1 $\pm$ 36.3 μg/L (median: 55.1 μg/L, ranging from 4.8 to 205.4 μg/L), and the average HHg was 16.8 $\pm$ 10.3 μg/g (median: 15.7 μg/g, ranging from 0.2 to 58.3 μg/g). The average percentage of MeHg was 86.8%, ranging from 75.2% to 94.3%. Men had significantly higher HHg levels (mean: 18.7 $\pm$ 11.2) than women (mean: 15.2 $\pm$ 9.1) (Mann–Whitney U, $P = 0.001$), but no significant difference was observed for BHg. There was a strong correlation between BHg and HHg concentrations ($r = 0.73$; $P < 0.0001$).

Table 2
Socio-demographic characteristics of the study population

Characteristics	Women		Men	
	n	%	*n*	%
Age				
15–24 years	61	25.1	51	23.6
25–34 years	58	23.9	45	20.8
35–44 years	51	21.0	47	21.8
45–54 years	27	11.1	25	11.6
55–64 years	23	9.5	27	12.5
⩾65 years	23	9.5	21	9.7
Alcohol consumption				
Drinks	79	32.6	125	58.1
No longer drinks	33	13.6	45	20.9
Never drank	130	53.7	45	20.9
Smoking habits				
Smoker	51	21.1	74	34.4
No longer smokes	49	20.2	59	27.4
Never smoked	142	58.7	82	38.1
Education				
No formal education	21	8.7	29	13.6
Elementary school (1–8 years)	206	85.5	175	81.8
High school and more (⩾9 years)	14	5.8	10	4.7
Born in Pará State	198	83.5	172	81.9
Location				
On the Tapajós River	172	70.8	144	66.7
On an tributary	71	33.3	72	33.2

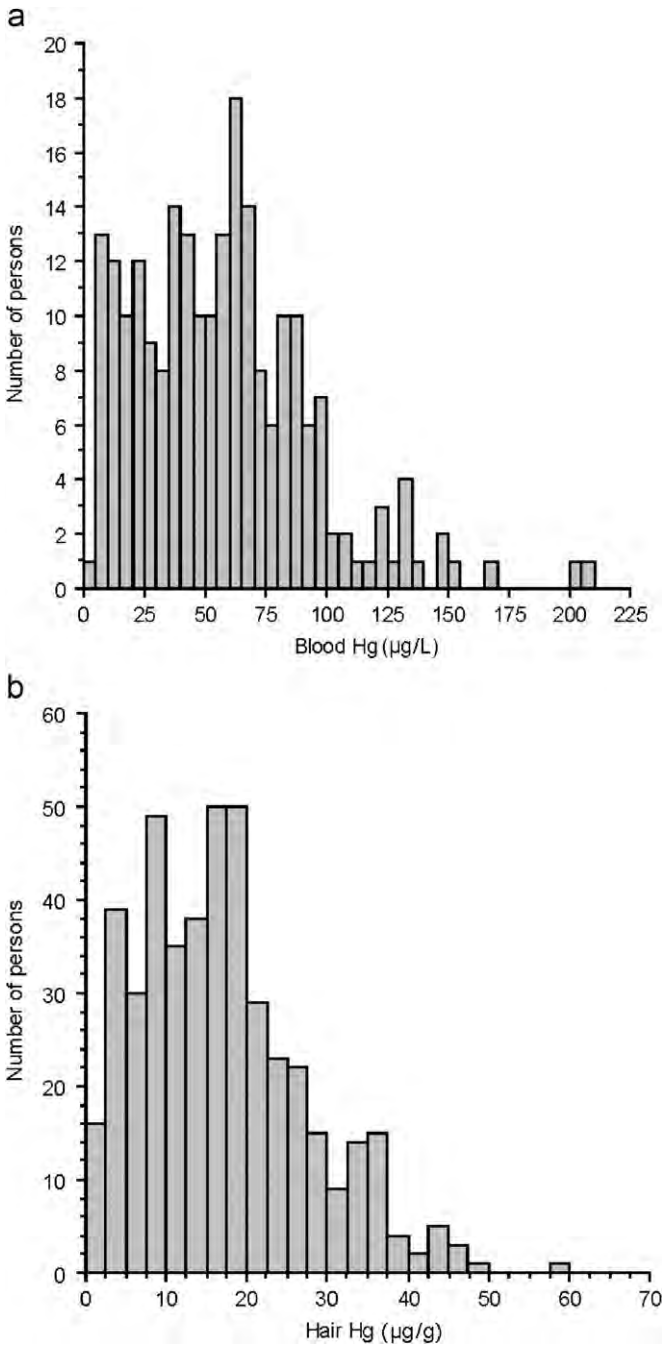

Fig. 2. Distribution of blood (A) and hair (B) total Hg concentrations for the study population.

In this survey, 457 persons consumed at least one meal with fish over the preceding seven days, making up 99.6% of the study population. Of these, 345 persons consumed at least one meal containing a carnivorous species (75.2%), whereas 393 persons ate at least one fish meal containing a non-carnivorous species (85.6%). In all, participants had consumed an average of 6.6 fish meals/week, ranging from

Table 3
Frequency of reports for fish most frequently eaten over the preceding 7 days

Fish species	Feeding habits[a]	Number of fish meals	%
Aracu (*Shizodon* sp.)	n-c	696	23.0
Pescada (*Plagioscion* sp.)	c	602	19.9
Caratinga (*Geophagus* sp.)	n-c	375	12.4
Tucunaré (*Cichla* sp.)	c	291	9.6
Jaraqui (*Semaprochilodus* sp.)	n-c	160	5.3
Pacu (*Myears lossoma* sp.)	n-c	155	5.1
Flexeira (*Hemiodus ocellatus*)	n-c	76	2.5
Branquinha (*Curimata amazonica*)	n-c	62	2.0
Piranha (*Sarrasalmus* sp.)	c	81	2.7
Others	—	529	17.5
Total	—	3027	100

[a]c, carnivorous; n-c, non-carnivorous.

0 to 19 meals/week. Table 3 shows the fish species most frequently eaten over the preceding 7-day period. Carnivorous fish made up an average of 43.5% of the fish diet, ranging from 0% to 100%. No associations were observed between total fish consumption and age, gender, schooling, cigarette smoking, and alcohol consumption. However, significant differences were observed between communities (Kruskal–Wallis, $P<0.0001$), as well as between persons originally from the Tapajós region and immigrants from northeast Brazil (Mann–Whitney U, $P<0.0001$). Those originally from the Tapajós region showed higher HHg levels (mean = 17.9 μg/g ± 10.1) compared to persons who had immigrated (mean = 12 μg/g ± 9.9).

Fig. 3(A and B) shows the relationships between weekly fish consumption (meals/week), BHg and HHg, respectively. Partial correlation analyses of fish consumption, categorized by feeding habits and Hg levels, show that the frequency of consumption of carnivorous fish is significantly correlated to both BHg and HHg ($r = 0.48$, $P<0.0001$ for BHg; $r = 0.34$, $P<0.0001$ for HHg), whereas the frequency of consumption of non-carnivorous fish is not related to BHg ($r = 0.01$, $P = 0.15$), and weakly correlated to HHg ($r = 0.14$, $P = 0.002$). This is reflected in individual species, with the highest correlations observed for large carnivorous fish such as *Pescada*, *Filhote* and *Piranha*. Despite its relatively high consumption, the carnivorous species *Tucunaré* was not significantly correlated to the bioindicators of Hg exposure, while *Aracu* and *Pacu* (non-carnivorous species) showed a weak correlation to HHg. These same relationships were observed when the fish were entered two-by-two into a multiple regression model.

A total of 40 fruit species were recorded during the survey, and 443 persons (96.5%) ate at least one of these fruits in the previous week. Three-hundred twenty-eight (328) persons (71.5%) reported eating bananas (*Musa* spp., Musaceae), the most consumed fruit, while 203 (44.2%) reported eating at least one orange (*Citrus* spp., Rutaceae).

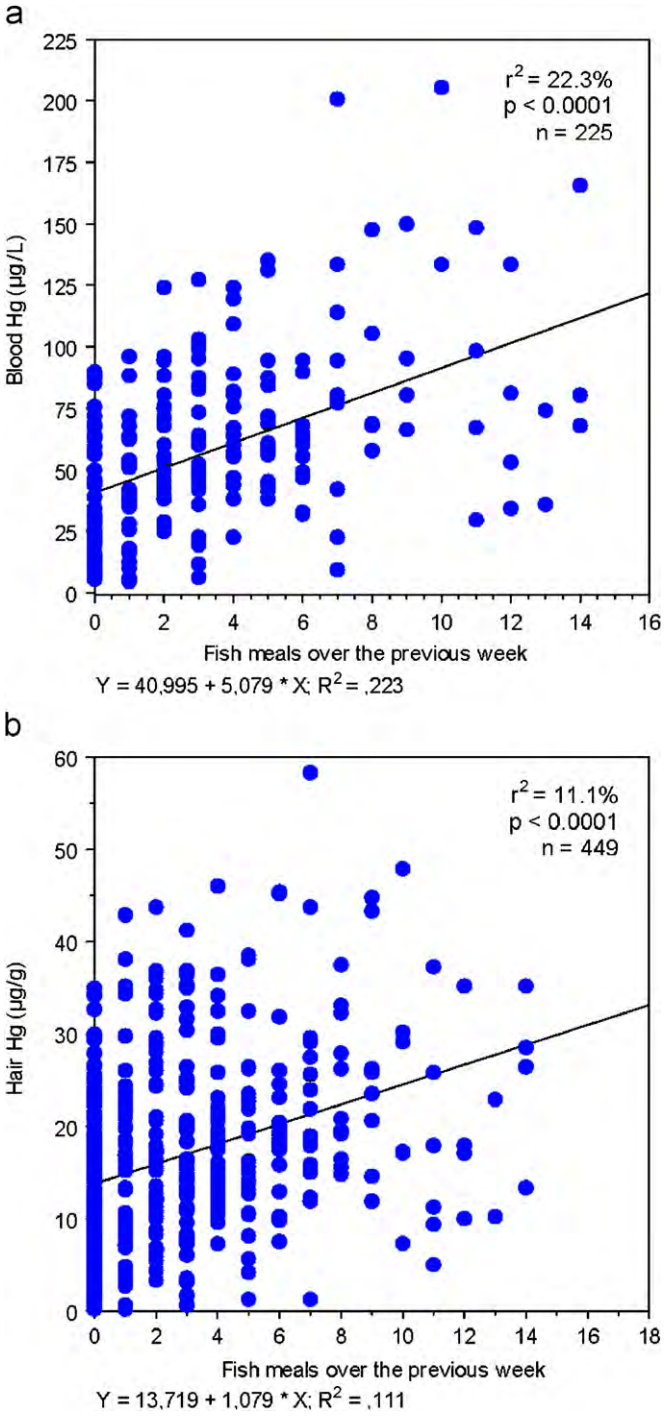

Fig. 3. The relationship between fish consumption (meals/week) and blood (A) and hair (B) total Hg concentrations.

Table 4 summarizes the distribution of persons with respect to fruit species consumption, as well as the frequency of reports for fruits most frequently eaten over the previous 7 days. Because of the important biodiversity in the Amazon, most fruits are consumed by only a small percentage of the participants, whereas only a few fruits are widely consumed by significant portions of the population.

On average, participants ate 11 fruits/week, ranging from 0 to 62 fruits/week. Although many types of fruit are

Table 4
Frequency of persons eating specific fruit and frequency of reports for fruit most frequently eaten over the previous 7 days

Fruit	Latin identification	Number of persons	Relative frequency (%)	Number of fruits	% total fruits
Bananas	*Musa paradisiaca*	328	71.5	1727	34.3
Oranges	*Citrus* sp.	203	44.2	973	19.3
Tucumã	*Astrocaryum aculeatum*	137	29.8	570	11.3
Guava	*Psidium guajava*	82	17.9	189	3.7
Passion fruit	*Passiflora* sp.	76	16.6	19	0.4
Jambo	*Eugenia* sp.	70	15.3	315	6.3
Avocado	*Persea Americana*	69	15.0	109	2.2
Ingá	*Inga* sp.	49	10.7	82	1.6
Brazil Nuts	*Bertholletia excelsa*	37	8.1	202	4.0
Others	—	300	65.4	845	16.8
Total	—	443	96.5	5031	100

Table 5
Results of multiple regression analyses for fish and fruit consumption in relation to BHg (μg/L) and HHg (μg/g) concentrations

Biological indicator	*n*	Regression estimates		Model R^2 (%)[a]
Blood total mercury (μg/L)		Carnivorous fish	Total fruit	
Women	111	4.8 ($P<0.0001$)	−0.7 ($P=0.0068$)	27.1
Men	114	6.8 ($P<0.0001$)	−0.4 ($P=0.0417$)	46.3
Total	225	5.6 ($P<0.0001$)	−0.5 ($P=0.0011$)	36.0
Hair total mercury (μg/g)				
Women	238	1.0 ($P<0.0001$)	−0.1 ($P=0.0276$)	16.1
Men	211	1.4 ($P<0.0001$)	−0.2 ($P=0.0058$)	21.6
Total	449	1.2 ($P<0.0001$)	−0.2 ($P=0.0002$)	21.0

[a]Adjusted factors in the regression equation: gender, cigarette smoking, non-carnivorous fish consumption.

seasonally available, the most frequently eaten are bananas and oranges. In this survey, we also observed a relatively high frequency of consumption of other regional fruits such as Tucumã (*Astrocaryum aculeatum*) and Jambo (*Eugenia* spp.), whereas Ingá (*Inga* spp., Leguminosae–Mimosoideae) was hardly consumed in this season. Total fruit consumption was weakly correlated with fish consumption ($r=0.1$; $P=0.003$), and inversely correlated with age ($r=-0.1$; $P=0.02$). It was also weakly correlated with schooling ($r=0.1$; $P=0.02$), but no relation was observed between fruit consumption and cigarette smoking or alcohol consumption. Similar to fish consumption, significant inter-village differences were observed (Kruskal–Wallis, $P=0.004$). Villagers living close to Itaituba City, the only urban center of the upper and middle Tapajós, reported lower fruit consumption as compared to villagers living in the proximity of Aveiro, a small town in the lower Tapajós.

Both fish and fruit entered significantly into the multivariate models explaining BHg and HHg; the regression estimates are presented in Table 5 for both women and men. The inverse relationship between fruit consumption and Hg levels remained significant, even when carnivorous and non-carnivorous fish were included separately. In addition to the overall effect of fruit consumption, multivariate models showed that some individual fruits presented enhanced negative regression estimates. Table 6 shows regression estimates for frequency of specific fruit consumption in multiple linear models with fish consumption and bioindicators of Hg exposure.

Fig. 4(A and B) illustrates the overall influence of these specific fruits (bananas, oranges, and jambos) on the relationship between fish consumption and Hg exposure. The regression lines are plotted for those with low fruit consumption ($\leqslant 3$ fruits/week; $n=64$), medium fruit consumption (>3 fruits/week $\leqslant 10$ fruits/week; $n=86$), and high fruit consumption (>10 fruits/week, $n=75$) in relation to BHg. For HHg, the low consumption group comprises 177 persons, the medium 169 persons, and the high consumers include 113 persons. Analysis of covariance showed that the intercepts of the three regression lines were similar, but their slopes were significantly different (Interaction term for BHg: $F=9.4$, $P=0.0001$; for HHg: $F=5.9$; $P=0.0029$). Thus, for low fruit consumers, each fish meal contributed 9.8 μg/L Hg increase in blood compared to only 3.3 μg/L Hg increase for the high fruit consumers. Similarly, each fish meal contributed approximately 1.7 μg/g Hg increase in hair of low fruit consumers as opposed to 0.5 μg/g increase in hair of high fruit consumers.

Most sociodemographic features such as age, schooling, cigarette smoking, and alcohol consumption were similar between low and high fruit consumers, while some slight differences were observed for a limited number of variables (Table 7). It is interesting to note that high fruit consumers ate more carnivorous fish.

Table 6
Regression estimates for frequency of specific fruit consumption (fruits/week) in multiple linear models with fish consumption (meals/week) as independent variable and bioindicators of Hg exposure

Biological indicator Fruits	Regression estimates		Model R^2 (%)[a]
Blood total mercury (μg/L)	Carnivorous fish	Fruit	
Oranges	5.3 ($P<0.0001$)	−1.6 ($P = 0.0006$)	36.2
Jambos	4.9 ($P<0.0001$)	−1.8 ($P = 0.0245$)	38.9
Hair total mercury (μg/g)			
Oranges	1.0 ($P<0.0001$)	−0.2 ($P = 0.0440$)	23.3
Bananas	1.0 ($P<0.0001$)	−0.2 ($P = 0.0246$)	23.0

[a]Adjusted factors in the regression equation: gender, cigarette smoking, non-carnivorous fish consumption, community.

4. Discussion

The results of the present study show a clear association between fruit consumption and lower Hg levels in this population, thus confirming the findings of our hypothesis-generating study conducted among 26 riparian women in the Amazon (Passos et al., 2003). This protective effect of fruit consumption against Hg exposure via dietary intake of fish is observed both for women and men; it is present in all categories of age and schooling, and occurs independently of other factors with a potential to influence Hg exposure, such as cigarette smoking and alcohol consumption.

A plausible explanation for the findings of this study is that the soluble dietary fiber content as well as other prebiotic nutrients of fruits could be interfering with absorption at the gastrointestinal tract. Indeed, demethylation of MeHg by microflora in the gut is a key and probably a rate-determining process in the removal of MeHg from the body, even though the microbes involved have not been identified nor have the biochemical mechanisms of cleavage of the carbon–mercury bond (Clarkson, 2002). A number of studies have suggested that the demethylation process in the intestine might well constitute an important site for interaction between diet and MeHg accumulation in the body (Chapman and Chan, 2000), the fiber content of the diet having already been shown to affect the excretion rate of MeHg (Rowland et al., 1986). Dietary elements have important effects on the metabolic activity of the intestinal flora (Gibson et al., 2004; Rowland, 1988), including a number of the carbohydrates present in significant amounts in several fruits and vegetables, which are able to stimulate the growth and/or activity of intestinal bacteria associated with health and well-being (Roberfroid, 2005). The effect of fruit consumption on these processes might explain, at least in part, why there is such a broad range of biologic half-times reported for adults exposed to MeHg.

The substantial inverse relation between Hg levels and consumption of oranges, which are known to present high levels of ascorbic acid (vitamin C), is particularly interesting since the role of this nutrient on MeHg exposure and toxicity has been controversial. Although Vitamin C has been implicated in the enhancement of MeHg toxicity (Murray and Hughes, 1976; cited in NRC, 2000), because of its strong reducing capacity, it is supposed to have potent detoxifying properties and has been used in cases of intoxication by heavy metals, including Hg. Sharma and colleagues (1982) demonstrated that ascorbic acid mediated a small but significant degradation of MeHg to inorganic mercury. Also, a more recent study concluded that ascorbic acid prevents mercury-induced genotoxicity in blood cultures due to its probable nucleophilic and detoxifying nature (Rao et al., 2001). In addition to ascorbic acid, oranges are also excellent sources of flavonoids and soluble dietary fiber.

Despite a positive relation between cigarette smoking and Hg levels observed in this population, the influence of fruit consumption remained unchanged. It is known that smokers have lower antioxidant status than non-smokers, but fruit consumption leads to a higher antioxidant status (Dietrich et al., 2003), which might explain the unchanged effect of fruit consumption. Indeed, one of the properties of several antioxidants particularly abundant in fruits is that they can form complexes with reactive metals, thus reducing their absorption (Bravo, 1998). Furthermore, the effect of fruit consumption also remained unchanged despite inter-village differences in terms of fruit consumption. Such regional differences probably reflect the fact that villagers near Itaituba City often buy fruit in the market, whereas those in more remote villages in lower Tapajós acquire fruit more often from their own home gardens.

Over these last years, diet of fish-eating communities has been the subject of much debate because of concerns about the potential health risks of MeHg exposure and, on the other hand, the public health implications of a diminished fish consumption (Arnold et al., 2005; Egeland and Middaugh, 1997; Myers et al., 2000; Weihg and Grandjean, 1998). Indeed, decreases in traditional food use has already been shown to affect diet quality and even to contribute to a number of diet-related health problems in indigenous peoples of Arctic Canada (Receveur et al., 1997). It is interesting that until recently the on-going birth cohort studies of heavy fish consumers of the Seychelles Islands in the Indian Ocean did not reveal adverse effects of MeHg, and some results even indicated beneficial outcomes

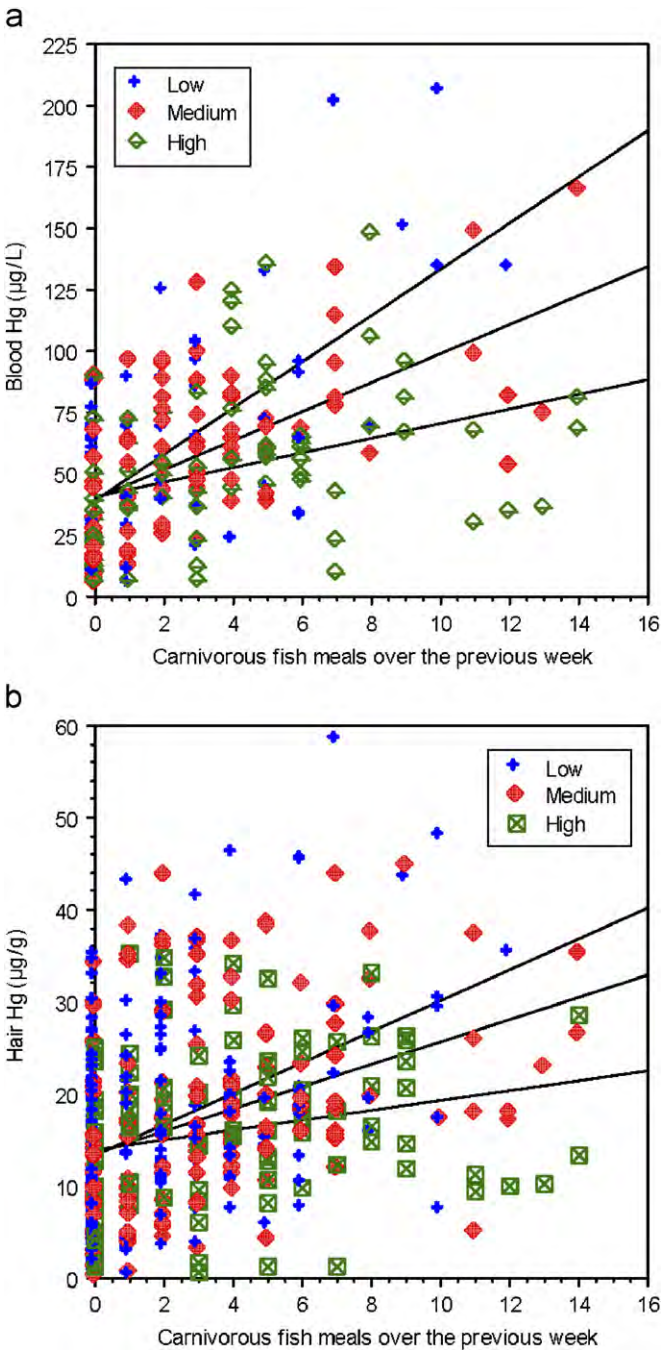

Fig. 4. The influence of fruit consumption on the relationship fish consumption (meals/week) and blood Hg levels (A), and HHg levels (B).

that correlate with Hg levels during pregnancy; the authors suggest a potential role of micronutrients in fish as a possible explanation for such findings (Clarkson and Strain, 2003). The importance of maintaining fish consumption when intervening to reduce Hg exposure in fish-eating populations was stressed by the Joint Expert Committee on Food Additives and Contaminants (JECFA) under the Food and Agriculture Organization (FAO) and the World Health Organization in their recent recommendations for tolerable daily maximum intake for Hg in pregnant/childbearing age women (WHO, 2003).

Table 7
Characteristics of fruit consumers according to their level of consumption

Characteristics	Low consumers[a] $n = 177$	Medium consumers[a] $n = 169$	High consumers[a] $n = 113$
Regional distribution			
Upriver (*Itaituba*)	97 (54.8)	78 (46.2)	38 (33.6)
Midriver (*Brasília Legal*)	37 (20.9)	18 (10.7)	6 (5.3)
Downriver (*Aveiro*)	43 (24.3)	73 (43.2)	69 (61.1)
Gender			
Women	98 (55.4)	97 (57.4)	47 (41.6)
Men	79 (44.6)	72 (42.6)	66 (58.4)
Fish consumption (meals/week)			
Carnivorous fish	2.1±2.7	3.2±3.2	3.8±3.6
Non-carnivorous fish	3.8±4.0	3.8±3.5	3.2±2.9
Hg levels			
Blood (µg/L)	61.7±44.6	57.9±33.1	52.3±31.5
Hair (µg/g)	17.0±11.2	17.4±10.4	15.8±8.4

[a]Data presented as mean±standard deviation or number of persons (percentage).

In the Amazon, recent reports have criticized any eventual suggestion to restrict fish consumption in traditional populations, which rely on fish as the main source of animal protein and other essential nutrients, suggesting that despite high concentrations of MeHg in fish, daily consumption of this food in large amounts poses no health hazards (Dórea, 2003, 2004). Although these reports rightfully point out the public health issues involved in diminished fish consumption, a more comprehensive approach, which takes into account the different sources of pollution as well as the socio-cultural and economic aspects of agriculture and diet, is needed in order to achieve viable risk management in this region. In particular, deforestation should be better controlled, thereby limiting Hg leaching from soils. It will also be necessary to better understand the dynamics involved in methylation in the areas of fish capture and to improve knowledge on the role of other foods able to influence Hg absorption and metabolism.

In this context, the challenge to maintain fish consumption while reducing Hg exposure remains. The encouraging results of a first intervention, which aimed at shifting towards consumption of less contaminated fish species and its impact in lowering exposure in a village on the Tapajós river have been presented elsewhere (Mertens et al., 2005; Bahia et al., 2004; Mergler et al., 2001). Indeed, through education based on posters showing the status of Hg contamination in relation to the fish species, the change in diet habits resulted in a reduction of close to 40% of HHg levels (Lucotte et al., 2004). The findings of the present study confirm a relevant avenue that deserves to be further explored as a potential additional intervention strategy

aimed at achieving the short-term challenge of maintaining fish consumption while reducing Hg exposure in this Amazonian setting.

In public health, it is well known that fruits contain a variety of compounds that may slow or prevent chronic diseases through several possible mechanisms. Components in fruits thought to be associated with the reduction of these conditions include soluble and insoluble dietary fiber, antioxidant nutrients (vitamins C, E, selenium, β-carotene), as well as other phytonutrients including polyphenols, flavonoids, anthocyanins and carotenoids (Feeney, 2004). Our findings indicate that fruit consumption may also be protective against the bioaccumulation of Hg in human populations exposed via dietary intake of fish.

Certain methodological issues of the present study need to be considered. First, there is always a tradeoff between the amount of data that can be collected and the size of the population. In the Passos et al. (2003) study, we opted for a large amount of chronological data collected through food diaries (written record of the foods as they are eaten, thus minimizing under- or over-reporting due to recall bias), and sequential HHg analyses from a small female population in order to identify the relevant food items that could then be used in a study with a much larger population (Passos et al., 2004). For the present study, we used a cross-sectional design on a convenience sample of men and women villagers from numerous riparian communities, assessing fish and fruit consumption frequency through a 7-DDR, and measuring Hg levels both in recent and chronic bioindicators of exposure. While the 7-DDR has been shown to constitute a sensitive method to assess short-term food consumption (Hebert et al., 1997), because of its retrospective nature there might have been some level of under- or over-reporting due to recall bias, especially for food items only moderately consumed (Pereira and Koifman, 1999). In addition, although data collection on convenience samples has been shown to appropriately represent the underlying population in other settings (Kelly et al., 2002; Zelinski et al., 2001), this sampling strategy may have introduced some selection bias in the present study. We did, however, achieve a participation rate of 35.7% in this adult population, well represented in most age categories. Moreover, most characteristics of fruit consumers were well distributed in the three categories of fruit consumption.

Another limitation of the present study is that it did not allow us to examine some of the possible physiologic events that may be involved in the interactions between fruit nutrients and MeHg. Studies examining the use of chelating agents as an intervention strategy to reduce blood lead levels raised questions about whether the process of chelation causes potentially dangerous redistribution of lead to susceptible organs from those less susceptible to lead toxicity (Goyer et al., 1995). Further studies should therefore examine the effect of fruit consumption from a toxicokinetic viewpoint.

5. Conclusion

Despite some limitations, this study constitutes strong evidence that fruit consumption provides a protective effect against Hg exposure in Amazonian riparian communities, whose traditional diet is based on daily consumption of Hg-containing freshwater fish. The results of this epidemiologic study are consistent with our previous findings (Passos et al., 2003) in which 26 riparian women presented lower HHg levels associated with consumption of regional fruit. Even though we did not measure toxicological outcomes in this study, it is reasonable to hypothesize that villagers consuming fruit regularly would be less vulnerable to neurological and/or cardiovascular risks linked to chronic Hg exposure. Future studies should be conducted to identify the specific nutrients responsible for this protective effect and examine the pharmacokinetics involved in these relations.

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References

Afonne, O.J., Orisakwe, O.E., Obi, E., Dioka, C.E., Ndubuka, G.I., 2002. Nephrotoxic actions of low-dose mercury in mice: protection by zinc. Arch. Environ. Health 57 (2), 98–102.

Almeida, M.D., Lacerda, L.D., Bastos, W.R., Herrmann, 2005. Mercury loss from soils following conversion from forest to pasture in Rondônia, Western Amazon, Brazil. Environ. Pollut. 137, 179–186.

Amorim, M.I.M., Mergler, D., Bahia, M.O., Dubeau, H., Miranda, D., Lebel, J., Burbano, R.R., Lucotte, M., 2000. Cytogenetic damage related to low levels of methyl mercury contamination in the Brazilian Amazon. An. Acad. Bras. Cienc. 72 (4), 497–507.

Arnold, S.M., Lynn, T.V., Verbrugge, L.A., Middaugh, J.P., 2005. Human biomonitoring to optimize fish consumption advice: reducing uncertainty when evaluating benefits and risks. Am. J. Public Health 95 (3), 393–397.

Bahia, M.O., Corvelo, T.C., Mergler, D., Burbano, R.R., Lima, P.D.L., Cardoso, C.S., Lucotte, M., Amorim, M.I.M., 2004. Environmental biomonitoring using cytogenetic endpoints in a population exposed to mercury in the Brazilian Amazon. Environ. Mol. Mutagen. 44, 346–349.

Barghigiani, C., Ristori, T., 1994. Mercury levels in agricultural products of Mt. Amiata (Tuscany, Italy). Arch. Environ. Contam. Toxicol. 26, 329–334.

Bravo, L., 1998. Polyphenols: chemistry, dietary sources, metabolism, and nutritional significance. Nutr. Rev. 56 (11), 317–333.

Calabrese, E.J., 1978. Nutrition and Environmental Health. Wiley, New York, NY.

Caruso, 2007. Mercury exposure and ecosystem health in the Amazon. 〈http://www.unites.uqam.ca/gmf/caruso/caruso.htm〉.
Clarkson, T.W., 2002. The three modern faces of mercury. Environ. Health Perspect. 110 (Suppl. 1), 11–23.
Clarkson, T.W., Strain, J.J., 2003. Nutritional factors may modify the toxic action of methyl mercury in fish-eating populations. J. Nutr. 133, 1539S–1543S.
Cleary, D., 1990. Anatomy of the Amazon Gold Rush. University of Iowa Press, Iowa City, 245pp.
Chapman, L., Chan, H.M., 2000. The influence of nutrition on methyl mercury intoxication. Environ. Health Perspect. 108 (Suppl. 1), 29–56.
Cordier, C., Garel, M., Mandereau, L., Morcel, H., Doineau, P., Gosme-Seguret, S., Josse, D., White, R., Amiel-Tison, C., 2002. Neurodevelopmental investigations among methylmercury-exposed children in French Guiana. Environ. Res. 89, 1–11.
Dietrich, M., Block, G., Norkus, E.P., Hudes, M., Traber, M.G., Cross, C.E., Pacher, L., 2003. Smoking and exposure to environmental tobacco smoke decrease some plasma antioxidants and increase γ-tocopherol in vivo after adjustment for dietary antioxidant intakes. Am. J. Clin. Nutr. 77, 160–166.
Dolbec, J., Mergler, D., Passos, C.J.S., Morais, S.S., Lebel, J., 2000. Methyl mercury exposure affects motor performance of a riverine population of the Tapajós River, Brazilian Amazon. Int. Arch. Occup. Environ. Health 73, 195–203.
Dolbec, J., Mergler, D., Larribe, F., Roulet, M., Lebel, J., Lucotte, M., 2001. Sequential analysis of hair mercury levels in relation to fish diet of an Amazonian population, Brazil. Sci. Total Environ. 271, 87–97.
Dórea, J.G., 2003. Fish are central in the diet of Amazonian riparians: should we worry about their mercury concentrations? Environ. Res. 92, 232–244.
Dórea, J.G., 2004. Cassava cyanogens and fish mercury are high but safely consumed in the diet of native Amazonians. Ecotoxicol. Environ. Saf. 57, 248–256.
Dórea, J.G., Barbosa, A.C., Ferrari, I., Souza, J.R., 2003. Mercury in hair and in fish consumed by riparian women of the Rio Negro, Amazon, Brazil. Int. J. Environ. Health Res. 13 (3), 239–248.
Dórea, J.G., de Souza, J.R., Rodrigues, P., Ferrari, I., Barbosa, A.C., 2005. Hair mercury (signature of fish consumption) and cardiovascular risk in Munduruku and Kayabi Indians of Amazonia. Environ. Res. 97, 209–219.
Ebbestadt, V., Gunderson, Torgrimsen, T.A., 1975. Simple method for the determination of inorganic mercury and methylmercury in biological samples by flameless atomic absorption. Atom. Absorption Newsletter 14 (6), 142–143.
Egeland, G.M., Middaugh, J.P., 1997. Balancing fish consumption benefits with mercury exposure. Science 278 (5345), 1904–1905.
Egler, S.G., Rodrigues-Filho, S., Villas-Bôas, R.C., Beinhoff, C., 2006. Evaluation of mercury pollution in cultivated and wild plants from two small communities of the Tapajós gold mining reserve, Pará State, Brazil. Sci. Total Environ. 368, 424–433.
Fadini, P.S., Jardim, W.F., 2001. Is the Negro River Basin (Amazon) impacted by naturally occurring mercury? Sci. Total Environ. 275, 71–82.
Farella, N., Lucotte, M., Louchouarn, P., Roulet, M., 2001. Deforestation modifying terrestrial organic transport in the Rio Tapajós, Brazilian Amazon. Org. Geochem. 32, 1443–1458.
Farella, N., Lucotte, M., Davidson, R., Daigle, S., 2006. Mercury release from deforested soils triggered by base cation enrichment. Sci. Total Environ. 368, 19–29.
Feeney, M.J., 2004. Fruits and the prevention of lifestyle-related diseases. Clin. Exp. Pharmacol. Physiol. 31, S11–S13.
Fillion, M., Mergler, D., Passos, C.J.S., Larribe, F., Lemire, M., Guimarães, J.R.D., 2006. A preliminary study of mercury exposure and blood pressure in the Brazilian Amazon. Environ. Health 5, 29.
Gibson, G.R., Probert, H.M., Loo, J.V., Rastall, R.A., Roberfroid, M.B., 2004. Dietary modulation of the human colonic microbiota: updating the concept of prebiotics. Nutr. Res. Rev. 17, 259–275.
Gill, U.S., Schwartz, H.M., Bigras, L., 2002. Results of multiyear international inter-laboratory comparison program for mercury in human hair. Arch. Environ. Contam. Toxicol. 43, 466–472.
Goyer, R.A., Cherian, M.G., Jones, M.M., Reigart, J.R., 1995. Meeting report: role of chelating agents for prevention, intervention, and treatment of exposures to toxic metals. Environ. Health Perspect. 103 (11).
Grandjean, P., White, R.F., Nielsen, A., Cleary, D., Santos, E.C.O., 1999. Methyl mercury neurotoxicity in Amazonian children downstream from gold mining. Environ. Health Perspect. 107 (7), 587–591.
Guimarães, J.R.D., Fostier, A.H., Forti, M.C., et al., 1999. Mercury in human and environmental samples from two lakes in Amapá, Brazilian Amazon. Ambio 28 (4), 296–301.
Guimarães, J.R.D., 2001. Les processus de méthylation du mercure en milieu amazonien. In: Carmouze, J.P., Lucotte, M., Boudou, A. (Eds.), Le mercure en Amazonie: Rôle de L'homme et de L'environnement, Risques Sanitaires. IRD Éditions, Paris.
Harada, M., Nakanishi, J., Yasoda, E., Pinheiro, M.C.N., Oikawa, T., Guimarães, G.A., Cardoso, B.S., Kisaki, T., Ohno, H., 2001. Mercury pollution in the Tapajós River Basin, Amazon: mercury level of haid hair and health effects. Environ. Int. 27, 285–290.
Hebert, J.R., Ockene, I.S., Hurley, T.G., Luippold, R., Well, A.D., Harmatz, M.G., et al., 1997. Development and testing of a seven-day dietary recall. J. Clin. Epidemiol. 50 (8), 925–937.
Hylander, L.D.H., Silva, E.C., Oliveira, L.J., Silva, S.A., Kuntze, E.K., Silva, D.X., 1994. Mercury levels in Alto Pantanal: a screening study. Ambio 23, 478–484.
Imura, N., Naganuma, A., 1985. Mode of modifying action of selenite on toxicity and behavior of mercury and other metals. Nutr. Res. (Suppl. 1), 499–507.
Kelly, H., Riddell, M.A., Gidding, H.F., Nolan, T., Gilbert, G.L., 2002. A random cluster survey and a convenience sample give comparable estimates of immunity to vaccine preventable diseases in children of school age in Victoria, Australia. Vaccine 20, 3130–3136.
Lapina, V.A., Sheshko, P.M., Dontsov, A.E., 2000. Phytosorbent prepared from sunflower seed husks prevents mercuric chloride accumulation in kidney and muscle of adult rabbits. Arch. Environ. Health 55 (1), 48–50.
Lebel, J., Mergler, D., Lucotte, M., Amorim, M., Dolbec, J., Miranda, D., Arantes, G., Rheaulth, I., Pichet, P., 1996. Evidence of early nervous system dysfunctions in Amazonian populations exposed to low-level of methyl mercury. Neurotoxicology 17 (1), 157–168.
Lebel, J., Roulet, M., Mergler, D., Lucotte, M., Larribe, F., 1997. Fish diet and mercury exposure in a riparian Amazonian population. Water Air Soil Pollut. 97, 31–44.
Lebel, J., Mergler, D., Branches, F., Lucotte, M., Amorim, M., Larribe, F., Dolbec, J., 1998. Neurotoxic effects of low-level methyl mercury contamination in the Amazonian Basin. Environ. Res. 79, 20–32.
Levander, O.A., Cheng, L., 1980. Micronutrient interactions, vitamins, minerals, and hazardous elements. Ann. NY Acad. Sci. 1, 355–372.
Lucotte, M., Davidson, R., Mergler, D., St-Charles, J., Guimarães, J.R.D., 2004. Human exposure to mercury as a consequence of landscape management and socio-economic behaviors. Part I: The Brazilian Amazon Case Study. In: Proceedings of the Seventh International Conference on Mercury as a Global Pollutant. RMZ-M&G: vol. 51, pp. 668–672.
Malm, O., Pfeiffer, W.C., Bastos, W.R., Souza, C.M.M., 1989. Utilização do acessório de geração de vapor frio para investigação do mercúrio em amostras ambientais por espectrofotometria de absorção atômica. Cienc. Cult. 41, 88–92 (In Portuguese).
Malm, O., Pfeiffer, W.C., Souza, C.M.M., Reuther, R., 1990. Mercury pollution due to gold mining in the Madeira river basin, Brazil. Ambio 19, 11–15.
Mergler, D., Boischio, A.A., Branches, F., Morais, S., Passos, C.J., Gaspar, E., Lucotte, M., 2001. Neurotoxic sequelae of methyl mercury exposure in the Brazilian Amazon: a follow-up study. In: Proceedings of the Sixth International Conference on Mercury as a Global Pollutant, October, Minamata, Japan, pp. 15–19.

Mertens, F., Saint-Charles, J., Mergler, D., Passos, C.J., Lucotte, M., 2005. A network approach for analysing and promoting equity in participatory ecohealth research. EcoHealth 2, 113–126.

Murray, D.R., Hughes, R.E., 1976. The influence of dietary ascorbic acid on the concentration of mercury in guinea-pig tissues. Proc. Nutr. Soc. 35 (3), 118A–119A.

Myers, G.J., Davidson, P.W., Cox, C., Shamlaye, C., Cernichiari, E., Clarkson, T.W., 2000. Twenty-seven years studying the human neurotoxicity of methyl mercury exposure. Environ. Res. 83, 275–285.

National Research Council, 2000. Toxicological Effects of Methyl Mercury. National Academy Press, Washington, DC, 344pp.

Nriagu, J.O., Pfeiffer, W.C., Malm, O., Sousa, C.M.M., Mierle, G., 1992. Mercury pollution in Brazil. Nature 356, 389.

Passos, C.J., Mergler, D., Gaspar, E., Morais, S., Lucotte, M., Larribe, F., de Grosbois, S., 2001. Characterization of the diet of a riverside population in the Brazilian Amazon. Rev. Saúde Ambiente 4 (1/2), 72–84 (In Portuguese).

Passos, C.J., Mergler, D., Gaspar, E., Morais, S., Lucotte, M., Larribe, F., Davidson, R., de Grosbois, S., 2003. Eating tropical fruit reduces mercury exposure from fish consumption in the Brazilian Amazon. Environ. Res. 93, 123–130.

Passos, C., Mergler, D., Larribe, F., 2004. Response to "Fruits, fish, and mercury: further considerations". Environ. Res. 96, 102–108.

Peraza, M.A., Ayala-Fierro, F., Barber, D.S., Casares, E., Rael, L.T., 1998. Effects of micronutrients on metal toxicity. Environ. Health Perspect. 106 (Suppl. 1), 203–216.

Pereira, R.A., Koifman, S., 1999. Using food frequency questionnaire in past dietary intake assessment. Rev. Saúde Pública 33 (6), 610–621 (In Portuguese).

Rao, M.V., Sharma, P.S.N., 2001. Protective effect of vitamin E against mercuric chloride reproductive toxicity in male mice. Reprod. Toxicol. 15, 705–712.

Rao, M.V., Chinoy, N.J., Suthar, M.B., Rajvanshi, M.I., 2001. Role of ascorbic acid on mercuric chroride-induced genotoxicity in human blood cultures. Toxicol. In Vitro 15, 649–654.

Receveur, O., Boulay, M., Kuhnlein, HV., 1997. Decreasing traditional food use affects diet quality for Adult Dene/Métis in 16 communities of the Canadian Northwest Territories. J. Nutr. 127, 2179–2186.

Roberfroid, M.B., 2005. Introducing inulin-type fructans. Br. J. Nutr. 93 (Suppl. 1), S13–S25.

Roulet, M., Lucotte, M., Saint-Aubin, A., Tran, S., Rhéault, I., Farella, N., De Jesus da Silva, E., Dezencourt, J., Passos, C.J.S., Santos Soares, G., Guimarães, J.R.J., Mergler, D., Amorim, M., 1998. The geochemistry of Hg in Central Amazonian soils developed on the Alter-do-Chão formation of the lower Tapajós river valley, Pará state, Brazil. Sci. Total Environ. 223, 1–24.

Roulet, M., Lucotte, M., Farella, N., Serique, G., Coelho, H., Passos, C.J.S., de Jesus da Silva, E., de Andrade, P.S., Mergler, D., Guimaraes, J.R.D., Amorim, M., 1999. Effects of recent human colonization on the presence of mercury in Amazonian ecosystems. Water Air Soil Pollut. 112, 297–313.

Roulet, M., Lucotte, M., Canuel, R., Farella, N., Courcelles, M., Guimarães, J.R.D., Mergler, D., Amorim, M., 2000. Increase in mercury contamination recorded in lacustrine sediments following deforestation in the central Amazon. Chem. Geol. 165, 243–266.

Rowland, I.R., Mallett, A.K., Flynn, J., Hargreaves, R.J., 1986. The effect of various dietary fibers on tissue concentration and chemical form of mercury after methylmercury exposure in mice. Arch. Toxicol. 59, 94–98.

Rowland, I.R., 1988. Factors affecting metabolic activity of the intestinal microflora. Drug Metab. Rev. 19 (3–4), 243–261.

Santos, E.C.O., Rosa, J.F.T., Jesus, I.M., Loureiro, E.C.B., 1992. A saúde das populações da Amazônia Brasileira. In: Yarzabal, L., Espinal y, C., Aragon, L.E. (Eds). Enfoque Integral de la Salud Humana em la Amazônia, Unamaz, pp. 95–156.

Santos, L.S.N., Muller, R.C.S., Sarkis, J.E.S., Alves, C.N., Brabo, E.S., Santos, E.O., Bentes, M.H.S., 2000. Evaluation of total mercury concentrations in fish consumed in the municipality of Itaituba, Tapajós River Basin, Pará, Brazil. Sci. Total Environ. 261, 1–8.

Sharma, D.C., Davis, P.S., Sharma, P.K., 1982. Effect of ascorbic acid on biotransformation and modification of the toxicity of mercurials in goldfish (*Carassius auratus*). Experientia 38 (5), 565–567.

Silva, I.A., Nyland, J.F., Gorman, A., Perisse, A., Ventura, A.M., Santos, E.C.O., Souza, J.M., Burek, C.L., Rose, N.R., Silbergeld, 2004. Mercury exposure, malaria, and serum antinuclear/antinucleolar antibodies in Amazon populations in Brazil: a cross-sectional study. Environ. Health 3, 11.

Silva, D.S., Lucotte, M., Roulet, M., Poirier, H., Mergler, D., Crossa, M., 2006. Mercury in fish of the Tapajós River in the Brazilian Amazon. InterfacEHS 1 (1) art 6.

Silva-Forsberg, M.C., Forsberg, B.R., Zeidemann, V.K., 1999. Mercury contamination in humans linked to river chemistry in the Amazon basin. Ambio 28 (6), 519–521.

Ursinyová, M., Hladiková, V., Uhnák, J., Kovacicová, J., 1997. Toxic elements in environmental samples from selected regions in Slovakia. Bull. Environ. Contam. Toxicol. 58, 985–992.

Usuki, F., Yasutake, A., Umehara, F., Tokunaga, H., Matsumoto, M., Eto, K., Ishiura, S., Higuchi, I., 2001. In vivo protection of a water-soluble derivative of vitamin E, Trolox, against methyl mercury-intoxication in the rat. Neurosci. Lett. 304, 199–203.

Weihg, P., Grandjean, P., 1998. Methyl mercury risks. Science 279 (5351), 635.

Whanger, P.D., 1992. Selenium in the treatment of heavy metal poisoning and chemical carcinogenesis. J. Trace Elem. Electrol. Health Dis. 6, 209–221.

WHO, 2003. World Health Organization, Joint FAO\WHO Expert Committee on Food Additives JECFA/61/SC.

Yokoo, E.M., Valente, J.G., Grattan, L., Schimidt, S.L., Platt, I., Silbergeld, E.K., 2003. Low-level methyl mercury exposure affects neuropsychological functions in adults. Environ. Health 2, 8.

Zelinski, E.M., Burnight, K.P., Lane, C.J., 2001. The relationship between subjective and objective memory in the oldest old: comparisons of findings from a representative and a convenience sample. J. Aging Health 13 (2), 248–266.

Environmental concerns of desalinating seawater using reverse osmosis

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This Critical Review on environmental concerns of desalination plants suggests that planning and monitoring stages are critical aspects of successful management and operation of plants. The site for the desalination plants should be selected carefully and should be away from residential areas particularly for forward planning for possible future expansions. The concerning issues identified are noise pollution, visual pollution, reduction in recreational fishing and swimming areas, emission of materials into the atmosphere, the brine discharge and types of disposal methods used are the main cause of pollution. The reverse osmosis (RO) method is the preferred option in modern times especially when fossil fuels are becoming expensive. The RO has other positives such as better efficiency (30–50%) when compared with distillation type plants (10–30%). However, the RO membranes are susceptible to fouling and scaling and as such they need to be cleaned with chemicals regularly that may be toxic to receiving waters. The input and output water in desalination plants have to be pre and post treated, respectively. This involves treating for pH, coagulants, Cl, Cu, organics, CO_2, H_2S and hypoxia. The by-product of the plant is mainly brine with concentration at times twice that of seawater. This discharge also includes traces of various chemicals used in cleaning including any anticorrosion products used in the plant and has to be treated to acceptable levels of each chemical before discharge but acceptable levels vary depending on receiving waters and state regulations. The discharge of the brine is usually done by a long pipe far into the sea or at the coastline. Either way the high density of the discharge reaches the bottom layers of receiving waters and may affect marine life particularly at the bottom layers or boundaries. The longer term effects of such discharge concentrate has not been documented but it is possible that small traces of toxic substances used in the cleaning of RO membranes may be harmful to marine life and ecosystem. The plants require saline water and thus the construction of input and discharge output piping is vital. The piping are often lengthy and underground as it is in Tugun (QLD, Australia), passing below the ground. Leakage of the concentrate *via* cracks in rocks to aquifers is a concern and therefore appropriate monitoring quality is needed. Leakage monitoring devices ought to be attached to such piping during installation. The initial environment impact assessment should identify key parameters for monitoring during discharge processes and should recommend ongoing monitoring with devices attached to structures installed during construction of plants.

1. Introduction

Almost all of the potable water required in the world today is supplied by surface water and groundwater resources.[1] Higher demands for potable water has led to excessive use and thus lowered the levels of surface water and ground water availability in many areas.[2,3] Increasing population particularly in coastal regions in different countries around the world has lowered the ground water table due to excessive pumping of ground water causing saline intrusion in countries such as Vietnam, Bangladesh, India and Florida state (US).[4–7] Erratic weather patterns linked to global climatic changes seems to have affected rainfall volume and pattern causing drought conditions in some parts of the world such as Australia. The extreme shortage of potable water has made countries rethink their potable water supply policies; for example, US and Australia are both considering alternatives of potable water supply.[8–10] A method exploited in many arid countries is desalination of seawater. Seawater is freely available and exists close to coastal lands where around 39% of the world's population reside, hence desalination of sea water can be an attractive and logical option for alternative potable water supply.[3,5,11]

Many countries in the Middle East, North Africa and Central Asia rely almost entirely on desalination for their potable water needs.[3,5,12] Indeed, it is proven technology and has helped alleviate freshwater scarcity in the Middle East for more than 20 years.[1,13] Despite the high energy demands, capital costs and environmental concerns, desalination appears to be a saviour for low rainfall occurring countries such as Australia. Although the negative impacts hve been reported at existing plants, equally positive aspects exist in that desalination aids and maintains industry, agricultural production, and helps preserve existing natural water resources. The

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pumping of seawater causes not only coning but also lowers close by seawater levels thus helping restrict saline intrusion into coastal aquifers.[3] However, environmental concerns such as emission of pollutants into the atmosphere, noise, and pollution caused by discharge of concentrates are important considerations and should be investigated before the desalination option is undertaken.[14]

2. Australian context

In the past, Middle Eastern gulf countries rich in fossil fuels preferred to build distillation type evaporative methods for desalination but development of better technology has shifted the preference towards the relatively cleaner and cheaper option of RO. The RO process has been used in the past mostly in inland plants treating brackish water that has much lower total dissolved solids (1000–10 000 ppm) than seawater (33 000–35 000 ppm). An RO plant has recently been built in Western Australia (WA) with a capacity of 130 000 m^3 d^{-1} (130 ML d^{-1}). A comparable USA plant is in Tampa (Florida) producing 100 000 m^3 d^{-1} and a similar capacity Askleon plant is in Israel producing 120 000 m^3 d^{-1} (120 ML d^{-1}). Australia has a smaller plant in Bayswater, New South Wales with a capacity of 35 000 m^3 d^{-1} (35 ML d^{-1}). Presently, a new RO plant (1250 000 m^3 d^{-1} or 1250 ML d^{-1}) is being built in Tugun (Queensland), Australia.

A serious water crisis exists in Queensland with the state experiencing the lowest dam levels sufficient to supply the region possibly for another two years only. Extreme level 4 restrictions are presently in place to conserve water and help lower the 750 ML d^{-1} current demand. Conservation is an important strategy but there are longer time issues facing Queensland; it is prone to long drought conditions and its population is rapidly increasing. All states in Australia are facing similar problems in that WA's population is predicted to double in 2020. Mostly the surface and groundwater resources supply the potable water in WA, now the groundwater is not appropriate for potable use. Given that groundwater may be taken as a finite source, it is vitally important that Australian states develop sustainable potable water supply programs.[15] The clear inability to cope with the present shortages has led both Queensland and WA to build large desalination plants even though they have been opposed by environmental groups. The environmentalists argue that desalination is relatively expensive, pollutes the environment and long term impacts of the pollutants are as yet unknown.

This article reviews the RO process of desalinisation focusing on the environmental concerns and issues. The research completed on the existing plants are analysed and studied in terms of possible impacts on the environment. Possible consequences of pollutants in marine discharges and coastal groundwater pollution are examined in light of the Tugun 125 ML d^{-1} RO plant being built in coastal Queensland, Australia.

3. Desalination processes

Desalination is the process of removing dissolved salts from seawater, brackishwater, riverwater, or other water effluent. The process requires a vast amount of energy and was considered less viable in the 1970's when the energy consumption requirements were over 20 kW h m^{-3} (20 kW h to desalinate one cubic meter of water). The energy demands are much less today. Most plants require around 3–20 kW h m^{-3}; when the minimum theoretical energy required to convert seawater to potable water is 0.7 kW h m^{-3}.[3] As mentioned earlier, the most widely applied technologies fall into two categories:

- Distillation based thermal (*e.g.* multi-stage flash (MSF)/ multi-effect distillation (MED), mechanical vapour compression (MVC) and
- Membrane based methods (*e.g.* reverse osmosis (RO), electrodialysis (ED) and nanofiltration (NF)).

The MSF thermal method involves water evaporation that leaves behind the salt as concentrated brine. This method is mostly employed where fossil fuels are cheaply or readily available such as in the Middle East but evaporative methods are being replaced steadily by membrane methods.[3] The MED is a thermal method that takes place in a series of vessels or "effects" and reduces the ambient pressure in subsequent effects. The MSF, MED and MVC are thermal processes that produce distilled water. Typically this distillate is very pure with a TDS of 1–50 ppm.

The RO method involves the use of high pressure pumps in the order of 800 psi–1200 psi (5.51 MPa–8.27 MPa) forcing the feed water, salts are rejected from the membrane, and hence the separation is accomplished. The membrane removes such impurities providing very low TDS potable water. Other commonly used membrane methods are ED and NF.

ED is a method for desalination of sea water using a main electrochemical generator that has an anode compartment through which seawater is fed causing the formation in the solution of chlorates and perchlorates; the removal of the latter being effected by a potassium salt such as potassium bicarbonate. This is an electro-membrane process in which the ions are transported through a membrane from one solution to another under the influence of an electrical potential. The ED technique can be utilised to perform several general types of separations such as separation and concentration of salts, acids and bases from aqueous solutions or the separation and concentration of monovalent ions from multiple charged components or the separation of ionic compounds from uncharged molecules.

NF allows diffusion of organic compounds, and rejects some salts with low pressures being applied and is a process normally used for mildly salt tasting water, or as a water softening technique. The NF is a form of filtration that uses membranes to separate different fluids or ions. NF is typically referred to as "loose" RO due to its larger membrane pore structure when compared to the membranes used in RO, and allows more salt passage through the membrane.

Membranes used for NF are of cellulosic acetate and aromatic polyamide type having characteristics as salt rejections from 95% for divalent salts to 40% for monovalent salts and an approximate 300 molecular weight cut-off (MWCO) for organics.[16]

In this Critical Review, of most concern is the reverse osmosis method for desalination of seawater as it removes

chloride salts, pathogens and other contaminants and provides better recovery rates but it is often compared with MSF.

Mutlistage flash (MSF) and reverse osomosis (RO)

There are approximately 7500 desalination plants in operation throughout the world and most of these (about 60%) are located in the Middle East.[17] About 12% of the world's capacity is in America while the remaining plants are in Spain, India and a few other countries. In the Red Sea/ Gulf Region, there are 280 thermal desalination plants and about 112 RO plants with production capacity ranges from 425 000 to 6800 000 m^3 freshwater per day. The Middle East is nevertheless still the largest user of RO desalination plants with capacities over 100 000 $m^3\ d^{-1}$ (300 ML d^{-1}). Increasing use is noted in Europe, West Indies, Spain, North America and now Australia with plants of over 100 000 $m^3\ d^{-1}$ (100 ML d^{-1}) capacity.

The thermal desalination (MSF) is a high energy driven process supplied usually by auxiliary boilers that are in turn responsible for discharging pollutants such as CO_2, NO_x, SO_x. MSF plants also discharge concentrated brine. The higher temperatures involved in distillation type techniques are responsible for the hotter discharge concentrates.

The RO plants do not require as high energy demands but can be noisy due to the use of high pressure pumps. These plants are also responsible for the discharge of concentrated brine together with sludge. While both plants discharge chemical agents needed in the pre/post treatment of seawater and discharge, respectively, the RO plants require careful attention due to membrane fouling. A number of chemicals are used to remove fouling in RO but their use is limited in quantity and can be treated before discharge. The RO plants have higher recovery rates of around 30–50% when compared to MSF, which is around 10–30%.

The nature of effluent discharged in the environment by desalination processes depend on the type of process involved. In this Critical Review, the focus is on the RO plants and in particular the environmental impacts of the processes applied. However, aspects of MSF will be also discussed in the comparative analysis presented in the following. The RO method is particularly important to the Australian context since two large RO based plants will be fully operational by 2008.

4. RO treatment

Osmosis involves diffusion of solvent such as water through a semi-permeable membrane caused by a difference in chemical concentrations of solutions either side of the membrane. For example, salty water on one side has a greater chemical concentration than the fresh water on the other. The solutions equilibrate by allowing the solvent water molecules to pass through from the dilute side to the concentrated side. The diffusion of water continues until the solutions essentially equilibrate in concentration (allowing for resistance of the membrane) or when the salty water head starts exerting an opposite hydrostatic pressure large enough to limit further diffusion of water totally. A greater pressure than the sum of the osmotic pressure difference and the pressure loss of diffusion through the membrane can be applied to reverse the process and this is known as RO.

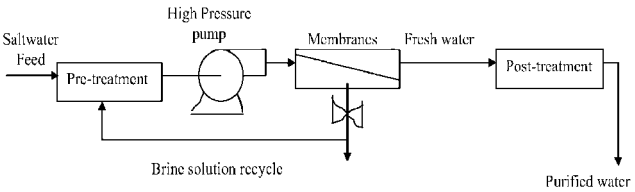

Fig. 1 Schematic diagram of an RO desalination treatment plant.

In the desalination plants, inlet seawater is treated and then pressurized (Fig. 1 and 2). The water from a pressurized saline solution is separated from the dissolved salts by forcing its flow through a water semi-permeable membrane. The liquid that passes through the membrane is referred to as permeate. The flow is caused by the pressure differential created between the feedwater and the permeate water (Fig. 1). Once water is separated, the remaining feedwater comes through as concentrate brine. Often a second or third stage treatment is included to capture lost water in this process. There is little heating or phase change in such a process and the major energy requirement is for the initial pressurization of the feedwater. For brackish water (1000–10 000 mg L^{-1} of minerals) the RO operating pressures range from 250–400 psi (1.72 MPa–2.75 MPa) while for seawater (10 000–37 000 ppm) desalination pressures required a range from 800–1200 psi (5.51 MPa–8.27 MPa).

Fig. 1 shows the feedwater being pumped into a closed container against the membrane to pressurize it. As the product water passes through the membrane, the remaining feedwater and brine solution becomes more concentrated. To reduce the concentration a portion of this concentrated feedwater–brine solution is withdrawn from the pressure vessel. For without such discharge, the concentration in the feedwater would continue to increase, requiring more energy inputs to overcome the increased osmotic pressure.

In the main, the reverse osmosis system consists of four major components/processes (see Fig. 1): pre-treatment, pressurization, membrane separation, and post-treatment.

Pretreatment: The feedwater is treated to be compatible before it goes to the membranes by removing suspended solids, adjusting the pH, and adding a threshold inhibitor to control scaling caused by constituents such as calcium sulfate.

Pressurization: The pump raises the pressure of the feedwater to an operating pressure, which is suitable for the membrane and the salinity of the feedwater.

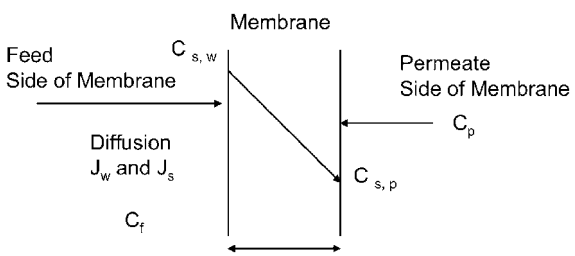

Fig. 2 Mathematical modelling of a RO membrane.

Separation: The permeable membranes inhibit the passage of dissolved salts while permitting the desalinated product water to pass through. Since no membrane is perfect in its rejection of dissolved salts, a small percentage of salt passes through the membrane and remains in the product water (acceptable drinking water levels require less than 500 total dissolved solids (TDS)). The smaller molecules such as CO_2 and H_2S may also pass through the membrane along with the product water. The RO membranes are available in a variety of configurations some spirally bound. The specific membrane and the nature and construction of the pressure vessel vary according to the different operating pressures used for the different types of feedwater (brackish or seawater).

Post-treatment stabilization: The product water from the membrane assembly usually requires pH adjustment and degasification before being transferred to the distribution system. In an aeration column, the pH of the product water is elevated from a value of approximately 5 to a value close to 7. In many cases, this water is discharged to storage for later use.

To determine efficiency, flow regime, solute concentrations and investigation of what if scenarios in RO process mathematical models may be developed. A simple model presented elucidates the underlying processes. After the treatment process, the feedwater is pumped at a particular pressure (Δp) through a channel with permeable membrane on one side and impermeable boundary on the other. A natural osmotic pressure exists due to the presence of the two sides of the membrane; and is dependent on the difference in chemical concentrations present. The osmotic pressure labelled $\Delta\pi$ is dependent on temperature, pressure and the membrane's ability to reject salts. The pressure difference allows the "permeate" or water to flow through the membrane toward a region of lower pressure. There is some resistance to this flow due to the membrane itself and depending on its properties the ability of a particular liquid to flow through is labelled A. In this manner a flow equation through the channel may be written as:

$$J_w = A(\Delta p - \sigma\Delta\pi) \quad (1)$$

where J_w is the flux of solvent through the membrane, A is the water permeability (this equation contains a negative sign, which is already included in water permeability A) and σ the reflection coefficient, which is approximately one in the case of high rejection membranes.[18] The solute flux (J_s) through the membrane is governed by the concentration difference between the membrane wall (C_M) from the feedwater and permeated product water that has passed through the membrane (C_P).

The solute flow can be written as

$$J_s = B(C_{s,M} - C_{s,P}) \quad (2)$$

The above two equations describe the major processes of solvent flow and solute transport often referred to as the solution–diffusion model. The parameters A and B are the water and solute permeabilities, respectively.[19] Further manipulations of these models can lead to the efficiency or recovery rate of RO by comparing the amount of solute passes or diffuses through the membrane with the concentration of solute remaining in the feedwater. In this manner, the permeate flow velocity in the channel can also be determined. The above models may be used to predict brine and chemical discharge concentrations in plants and appropriate measures may be undertaken for better management. It is clear that stringent planning and monitoring is needed when considering the costly desalination option and mathematical models may be useful in determining critical loads and in the conduction of risk analysis.

5. Planning and monitoring of plants

Some studies in the literature have attributed difficulties to inappropriate planning.[14] Before the construction begins an appropriate feasibility study should be conducted for the choice of a suitable site.[20] If the site chosen is close to residential areas, the visual and noise pollution may be a problem. Reports suggest that noise levels can be high due to the use of variable pressure pumps.[17,21] The site chosen should then be away from residential regions whenever possible. Moreover, most desalination plant sites are constructed close to coastal areas and therefore would diminish any visual and architectural beauty related to the area. Recreational activities such as fishing and boating are further restricted around the inlet/outlet areas.

Devising a monitoring plan for plants appear critical but it is often considered after the actual completion of the plant.[14] A number of monitoring devices often have to be installed in subsurface piping or attached structurally to inlet and outlet structures underground and such installations are only possible during construction of the desalination plants. Planners need to think about developing an environmental monitoring program much earlier in the process. In the main, the monitoring should address critical parameters or issues identified in the environmental impact study (EIS) such as temperature, density, hypoxia, chlorine and copper levels for example. The monitoring should include the measurement of the important parameters making certain they meet established guidelines. Essentially, environmental management plans are necessary during the plant's operation to ensure the plant is operating within set environmental standards.[22] Inadequate planning and/or monitoring can lead to a number of problems that are difficult to solve later such as redrilling to install sensors and other monitoring equipment.

Desalination plants require water intake structures and pipelines that can carry feedwater and discharge concentrate to and from sea, respectively. The Tugun plant piping is proposed to be built 50 m below ground level and material may leak through to the aquifer. As such, the coastal groundwater aquifers may be contaminated through leakage in the long inlet/outlet pipes. The outlet pipes contain discharge sludge that is usually highly concentrated brine but may also contain low concentrations of chemicals sometimes at elevated temperatures. Therefore, careful monitoring of the piping as well as flow processes is needed. Appropriate monitoring devices may be attached to fixed structures to ensure failsafe subsurface flow processes and thus should be considered before construction is completed.

Another aspect of the pollution is the disposal of brine to seawaters such as the ocean. If such discharge products are released into surface seawater, the properties of the concentrated discharge products including chemicals that are not treated may cause problems for the marine habitats and receiving water environments. This is mainly due to the higher density of concentrate discharge compared to seawater that generally sinks to the bottom layers.

Desalination projects require an environmental impact assessment (EIA) study and the EIA should identify all critical environmental parameters and evaluate potential impacts to air, land, and marine environments. There are five aspects to the impact of desalination plants on the environment.

- Adverse effect on land use: seashores serve as the sites for industrial plants and for pumping stations rather than for recreation and tourism.
- Impact on the aquifer: leakage from the pipes may result in penetration of salt water and therefore presents a danger to the aquifer.
- Impact on the marine environment: as a result of returning the concentrated brine to the sea.
- Impact of noise: desalination plants require high pressure pumps and turbines, which produces noise.
- Intensive use of energy: an indirect impact on the environment due to increase production of electricity.

The duty of environmental impact services (EIS) is to propose mitigation measures to reduce environmental impacts to safe levels but also discuss benefits the facility may offer to the community. Well designed mitigation measures will reduce possible problems associated with the facility in the future.[23]

6. By-products of desalination plants

As noted earlier, desalination plants generate two products; clean water and concentrate brine (that is, the reject or residual stream). It is important to realize that cost-effectiveness and concentrate brine discharge are obstacles in the widespread use of desalination. Clearly, appropriate brine disposal methods incorporated in the plant's design can reduce the concentrate's impact on the receiving waters and coastal groundwater aquifers.

6.1 Brine characteristics

The main by-product of desalination plants is brine, referred to as the concentrate. This concentrate is made up of liquid substances containing up to 20% of the treated water. TDS, temperature, and specific weight (density) are the key parameters of the concentrate. The TDS of brine concentrate is usually greater than 36 000 mg L^{-1} (sometimes greater than 40 000 mg L^{-1} in many states in the Middle East). At 50% recovery 70 000 mg L^{-1} TDS are produced. The concentrate may also contain some chemicals that are used in pre/post-treatment usually in cleaning processes. Characteristics of the generated concentrate depend on the type of desalination technology used. Table 1 shows characteristics of concentrates from various desalination plant types.[24,25]

The amount of concentrate produced from a desalination plant is a factor of the desalination recovery rate (that is, product water/feedwater). Usually the RO membrane based plants have a higher recovery rate than distillation plants resulting in higher salt concentration amounts in the concentrate. Table 1 shows that the concentrate produced from seawater reverse osmosis (SWRO) plants have up to two times more salt concentration than the receiving water, while the concentrate produced from a distillation process may only have 10% higher. In distillation processes, the system mixes the concentrate with (once-through) cooling water to dilute the salt concentration. Table 1 also shows that the concentrate from distillation processes tend to be typically warmer, 10–15 °F above the ambient water temperature. Concentrate temperature from the reverse osmosis process often remains at the ambient water temperature.[25]

As noted earlier, specific weight (or density) is a critical concentrate parameter and compared to freshwater, the concentrate has a higher density. When disposed into waters of lower salinity (lower density) the concentrate usually sinks to the bottom layers.[26] In contrast, typical discharge from wastewater treatment plants will float as the discharge density is normally less than the receiving water. The tendency of the concentrate to sink when interacting with the receiving water introduces problems for the marine environment in that the discharge may be hypoxic or contain traces of damaging chemicals. In some cases, desalination plants dilute the concentrate to reduce density before release. Blending is a process that mixes the concentrate with cooling water, feedwater, or other low TDS waters before disposal

6.2 Pre/post treatment

Pre-treatment can include chlorination, clarification, coagulation, acidification, and degasification. Pre-treatment is applied to feedwater to minimize algae growth, scaling, and corrosion of the plant generally. The chemical agents used in the process are important and should be monitored since some remain in the concentrate before disposal. Typical pre-treatment chemicals used in desalination plants are:

- NaOCl or free chlorine—prevents biological growth;

Table 1 Concentrate characteristics in desalination technologies (adapted from Younos[33])

	Plant type	BRO	SRO	MSF/MED
Feedwater	Input	Brackish (B)	Seawater (S)	Seawater (S)
Recovery	Output	60–85%	30–50%	15–50%
Temperature	Output	Ambient	Ambient	15–50% above ambient
Concentrate dilution/blending	Output	Possible, not typical	Possible, not typical	Typical, with cooling water
Final ratio-concentration	In/output	2.5–6.7	1.25–2.0	<1.15

[a] BRO = Brackish water reverse osmosis, SRO = Seawater reverse osmosis, MSF = Multistage flash evaporation, MED = Multiple effect distillation.

• $FeCl_3$ or $AlCl_3$-flocculation and removal of suspended matter from water;
• H_2SO_4 or HCl—pH adjustment;
• $NaHSO_3$—neutralizes chlorine remains in feedwater; and
• Various scale inhibitors—prevents scale formation on the pipes and membranes.

If an RO membrane becomes fouled or scaling occurs, the materials have to be removed and this is done *via* chemical cleaning with the use of various detergents. The type of chemicals used for cleaning depends on the type of membrane and for RO systems, chemical cleaning agents fall into the following categories:[27]

• Enzymes to break down bacterial slimes;
• Detergents and surfactants to resuspend particulate material and dissolve organic material;
• Biocides to kill bacteria;
• Chelators to remove scale;
• Acids to dissolve inorganics;
• Caustics to dissolve organic substances and silica.

The major pollutant of distillation processes is chlorine, which is added to prevent bio-fouling on heat exchanger surfaces. The two major pollutants in RO processes are chlorine and copper.

Chlorine. In RO plants, chlorine is also a common biocide. Most modern plants operate on polyamide membranes, which are sensitive to oxidizing chemicals such as chlorine. Treatment is typically required before the feedwater enters the RO unit. Chlorine is a strong oxidant and highly effective biocide and residual levels in the discharge may be toxic to marine life close to the discharge site. Following discharge, self-degradation and dilution lowers the environmental chlorine levels to lower concentrations but even such low concentrations are adverse to aquatic life.[17] Chlorine reacts with organic compounds in seawater forming a large number of chlorinated and halogenated organic by-products. Studies show that many of these compounds are carcinogenic or otherwise harmful to aquatic life.[17]

Chlorine is classified as a pollutant in the US and concentration limits are recommended by the Environmental Protection Agency (EPA) to avoid toxic conditions. For example, in saltwater, 0.013 ppm is allowed for the short term while 0.0075 ppm is considered safe for the longer term.[28] These restrictions can be met, for example, by limiting discharge concentrations to the same level. In some US states more stringent criteria have been established (California) such as zero tolerance; that is, the residual levels have to be totally treated.[28]

Due to environmental and health problems caused by residual chlorine and disinfection by-products, several alternative pre-treatment methods have been considered to replace chlorine in desalination plants. Ozone and monochloramine are some alternatives while ultraviolet light may be used instead of biocides to eliminate micro-organisms.

Copper. In most RO processes, non-metal equipment and stainless steels items are used. The discharge levels in RO usually refer to the brine not the total effluent, which is about one third brine and two thirds cooling water discharged. It is likely that the cooling water is contaminated but it is not included in copper load calculation generally. The copper load is based on brine contamination only thus resulting in a conservative estimate of copper. In contrast to chlorine loads, where the product/effluent ratio (1 : 9) is used since both the cooling water and desalination feed water are chlorinated, in the case of copper product/brine ratio of 1 : 2 is assumed. As before, a standard ratio between product capacity and chemical load is formed. Based on 30 g d^{-1} copper output per 1000 m^3 d^{-1}, the daily discharge amounts to 36 kg in the area studied.[28]

It is well known that copper is not the only corrosion product released in that nickel, chromium, molybdenum and iron are also important to consider. It should be noted that the mere presence of copper does not imply an adverse effect on the environment since copper is an essential micronutrient for many organisms but copper becomes toxic whenever excess amounts of it become biologically available. A low brine of approximately 15 ppb appears to reduce the risk of toxic conditions for aquatic life with dispersion further decreasing the dissolved copper levels.[29]

Clearly, pre- and post-treatments are required in RO processes, and in particular, the post-treatment is needed to treat excess carbon dioxide and oxygenate to compensate for the lack of oxygen in the discharge concentrate.[29] The degasification of CO_2 is also an issue since CO_2 aids global warming. The foul smell is at times noted in product water and this is due to hydrogen sulfide which is removed through aeration.[24] Oxygen is added to treat hypoxic conditions. Table 2 outlines the processes involved in pre-treatment and post-treatment of desalination plants.

In the USA the National Pollutant Discharge Elimination System (NPDES) program regulates concentrate discharge to surface waters. The NPDES requires Whole Effluent Toxicity (WET) testing of concentrate to determine potential impacts on aquatic species. When tested, several utilities in Florida that use membrane technologies failed WET tests for unknown reasons. Research to determine causes of failure by examining concentrate characteristics from nine utilities in Florida showed the presence of excessive ions.[24] Calcium and fluoride levels in concentrate were the major contributors.[24] In coastal areas, due to the dynamic nature of fresh water and saltwater interaction, the composition of brackish groundwater is not uniform or chemically balanced; while in

Table 2 Pre-treatment and post-treatment processes

Step no.	Pre-treatment	Post-treatment
1	Chlorination where biological growth may be present	Degasification for CO_2
2	Polymer additives used for scale control	Aeration to remove H_2S, adding O_2
3	For RO sometimes acid is used in addition to additives	For RO, pH adjustment required for corrosion protection
4	Dechlorination for some membrane processes where chlorination is used	

these waters, calcium carbonate and calcium sulfate were dominant over sodium chloride.

Pre-treatment prior to disposal consists of aeration, *i.e.*, adding oxygen to the concentrate, and degasification to remove hydrogen sulfide from the concentrate.[28] Using non-toxic additives and dechlorination techniques limits the toxic chemical concentrations that enter the environment. The need for these techniques is site-specific depending on the maximum concentrations of the additives and chlorine allowed in the discharge.

Antiscalants. Antiscalants are products used to prevent fouling of membranes and need to be present in both MSF and RO plants.[28] In the main, the outputs involve organics, carboxylic rich polymers such as polyacrilic acid and polymeric acid. It is usually assumed that about 2 ppm enters the receiving waters. The load from an RO is typically 6 kg d^{-1} per 1000 m^3 d^{-1}, a total of around 2257 kg d^{-1}.[28] While a daily load up to 9.4 tonnes of antiscalants by RO plants appears high the environmental risk of these substances is low when compared to chlorine and copper. Generally, the antiscalants are of low toxicity and their environmental fate involves significant dilution thus reducing possible ill effects. However, poor degradability is a major drawback in that polymaleic acid biodegrades slowly while polyacrilic acid is three times faster. Nonetheless, the antiscalants may limit availability of important trace metal ions in receiving waters.

6.3 By-product management options—brine disposal

At present, approximately 48% of desalination facilities in the US and most others including many of the Middle East states dispose their concentrates to surface waters.[28] Other concentrate disposal options include deep well injection, land application, evaporation ponds, brine concentrators, and zero liquid discharge (ZLD) technologies.[26] Only surface water type, deep injection and waste water treatment disposal methods are analysed here and considered important in the Australian context. In order to choose a method among those mentioned, a number of factors need consideration including volume or quantity of concentrate, quality of concentrate, location of desalination plant, and environmental regulations. Other factors that could be critical are public acceptance, total costs of operation, and future plant expansion.

Surface water disposal. The surface disposal methods include the surface water disposal and submerged disposal.[17] The most common way to dispose of the desalination plant concentrates is to dump them into the surface waters such as freshwater lakes or ponds, tidal streams and rivers, oceans, bays and estuaries. Clearly, the concentrate would somewhat pollute the disposed area often creating a plume in the waters.[17] The density of the concentrate would determine whether the plume caused by disposal sinks, floats, or stabilizes in surroundings waters. The waves, tides, bathymetry, currents, water depth determines whether dilution and general mixing occur but often the diluted plume may exist for a number of days possibly harming the ecosystem.[24]

Most countries have limits placed on such disposal into surface waters. For example, in the USA, Florida has placed its mixing zone limitations at 2625 ft for canals, rivers, and streams; and 31 acres for lakes, estuaries, bays, lagoons, and bayous; including 124 acres for oceans.[30] The WET test is used and if natural dilution is not appropriate for proper diffusion the special artificial ponds needs to be created for dilution. Clearly, the concentrate may be treated before discharge in that it can be diluted through blending or with the help of diffusers, within the standard mixing zones. Diffusers are jets that dilute the concentrate at the concentrate disposal outlet for maximum mixing. In the case of diffusers, the factors include the difference in densities between the concentrate and the receiving waters, momentum and velocity of the water at the outlet. Small-scale desalination plants studied in Florida, which dispose directly into the sea or use a short discharge pipe, showed no environmental impact on the animal and plant life near the outlet pipes.[24]

Submerged disposal. Submerged disposal is defined as the disposing of concentrate underwater, rather than disposing on the surface. Similar to surface disposals submerged disposal also occurs in tidal or estuarine environments. Disposal is done through the use of pipes far into the ocean in contrast with surface disposal that usually occurs closer to the coastline. Country regulations usually define certain zones in open oceans usually labelled the "allocated impact zones" and the water quality limits can be exceeded in such zones for non-toxic pollutants.[31] As noted earlier, the concentrate being of higher density usually sinks to the bottom of the ocean and creates a quantitative boundary where the salinity limits may be exceed regulated limits. In this case the dilution zone is understood to be the various vertical layers through which the concentrate passes through to reach the bottom.[31] Being at the bottom of the ocean the benthic marine organisms living at the sea bottom are clearly at risk mainly due to high salinity and low dissolved oxygen levels. Mickley[24] noted that long abdomen invertebrates are more sensitive to high salinities than short abdomen invertebrates in the bottom ocean conditions.

Clearly a number of factors need to be considered before deciding on the discharge method. For example, if the area is highly populated, coastline disposal may be a problem, because of the interference of the mixing zone with recreation close to the beach. This is especially noticeable on days when the sea is calm when little to no natural dilution occurs. Although models have been developed for US conditions, similar models for the Queensland of shore conditions particularly for the Tugun plant should be developed to investigate possible outcomes of such disposal methods.[31] Computer programs will allow prediction at different dilution/dispersion rates under local conditions and moreover suggest possible environmental effects of concentrate disposal.

Disposal to front of wastewater treatment plant. The other most common option is to dispose of the concentrate into existing waste water treatment plants.[32] The concentrate is dumped in the "front" or head works of a wastewater treatment plant or publicly owned treatment works.[24] There are however, a number of concerns with this method such as the effect of very high salinity levels on the performance of the biological treatment especially when the concentrate volume is

large; and the output of high TDS processed waste water in the plant effluent. In the end, these may lead to a reduction of plant treatment capacity as a whole but this option requires further research.

7. Summary and conclusions

The various studies and general literature reviewed suggests stringent planning and monitoring is a critical aspect for the successful management of desalination plants. The site for the desalination plants should be selected carefully and should be away from residential areas particularly for forward planning for possible future expansions. Difficulties experienced by existing plants were often attributed to inadequate planning or less detailed environmental impact studies. A feasibility study together with environmental impact assessments should be conducted by appropriate authorities in relation to the proposed desalination plant and site. The concerning issues identified from existing plants are noise pollution, visual pollution, reduction in recreational fishing and swimming areas, emission of materials into the atmosphere, and most importantly pollution caused by product discharge and types of disposal methods used. The RO method is the preferred option in modern times especially when fossil fuels are becoming expensive. The RO has other positives such as better efficiency (30–50%) when compared with distillation type plants (10–30%). However, the membranes in RO are susceptible to fouling and scaling and as such they need to be cleaned with chemicals regularly that may be toxic to receiving waters. Complex RO models exist that can predict concentrations, velocity and membrane adsorption and should be used to complement risk assessments in membrane based desalination plants. The input and output water to desalination plants have to be pre- and post-treated respectively. This involves treating for pH, coagulants, Cl, Cu, organics, CO_2, H_2S and hypoxia. The by-product is usually termed the concentrate containing mainly brine with concentration at times twice that of seawater. This discharge also includes traces of various chemicals used in cleaning including any anticorrosion products used in the plant. This discharge concentrate has to be treated to acceptable levels of each chemical before discharge but acceptable levels may vary depending on receiving waters and state regulations. The disposal is usually done on surface waters some times through surface piping while other times subsurface piping. Either way the high density of the discharge reaches the bottom layers of receiving waters and thus may affect marine life particularly at the bottom layers or boundaries. The longer term effects of such discharge concentrate has not been documented but it is possible that even small traces of toxic substances used in the cleaning of RO membranes may be harmful to marine life and the ecosystem generally. The plants require saline water input and discharge output piping. Such pipes are often lengthy and underground as it is in Tugun (QLD), more often than not passing below the existing coastal aquifers. Leakage of the concentrate *via* cracks in rocks to aquifers is a concern and therefore appropriate monitoring of the piping and aquifer water quality is needed. Importantly, leakage monitoring devices ought to be attached to such piping during installation. The initial environment impact assessment should be critical enough to identify key parameters for monitoring during discharge processes and should recommend ongoing monitoring with devices attached to structures installed during construction of plants.

In conclusion:

- The decision of when, how and which plant to build should be based on both environmental and socio-economical concerns;
- The sustainability of the plant must be considered in light of global climatic changes, sea level rise and possible expansion due to water demands;
- Discharge concentrate products should be critically monitored but sediment disturbance at the bottom of receiving waters tends to occur in oceans and thus should also be investigated;
- Damage by chlorine and copper appear to exist around outlets and later processes such as dilution, self-decomposition of chlorine and transport of copper into sediments appear to facilitate their fate; and
- Possible changes in flow and currents caused by concentration differences of discharge concentrates that are of much higher density should also be investigated.

The environmental lessons learned from longer term existing plants is a useful guide and is discussed here but much is still unknown about the longer term effect of the costs, energy use, emissions and discharges from such plants.

References

1 R. Semiat, *Desalination: Present and future*, International Water Resources Association Water International, March 2000, vol. 25(1), pp. 54–65.
2 O. K. Buros, *The ABCs of Desalting*, International Desalination Association, Massachusetts, USA, 1999.
3 M. Schiffler, Perspectives and challenges for desalination in the 21st century, *Desalination*, 2004, **165**, 1–9.
4 G. Bennett, J. Bredehoeft and L. H. Motz, *Salt water intrusion and the minimum aquifer level in the southern water use caution area*, Hydrologic Evaluation Section Southwest Florida Water Management District, August 2002.
5 H. El-Dessouky and H. Ettouney, *Teaching Desalination—A Multidiscipline Engineering Science*, Department of Chemical Engineering, College of Engineering and Petroleum, Kuwait University, Safat, Kuwait, 2002.
6 V. Post, *Groundwater salinization processes in the coastal area of the Netherlands due to transgressions during the Holocene*, Vincent Eduard Alexander Post, 2004.
7 G. A. Tularam, N. Surawski and R. Braddock, Capabilities of saltflow and Pde2d in modelling saltwater intrusion in coastal Australian lowlands, *Aust. Geomech. J.*, 2006, **41**(1), 73–78.
8 T. Winter, D. J. Pannell and L. McCann, *The Economics of Desalination and its Potential Application in Australia*, Agricultural and Resources Economics, University of Western Australia, Perth, WA 6009, Australia, 2001.
9 D. J. Pannell, Dryland Salinity: Economic, scientific, social and policy dimension, *Aust. J. Agric. Resour. Econom.*, 2001, **45**(4), 517–546.
10 Nuclear desalination, UIC Nuclear Issues Briefing Paper No. 74, October 2006.
11 G. L. Meerganz von Medeazza, *Desalination as a sustainable alternative to inter-basin water transfers?*, paper presented at the IV Congreso Ibérico del Agua, Tortosa, Spain, 8–12, 2004.
12 P. H. Gleick, *The Worlds Water: biennial report of fresh water resources 1998–1999*, Island Press, USA, 1998.
13 M. A. Fkirin and A. F. Al-Madhari, Prediction of time-varying dynamic processes, *Int. J. Qual. Reliab. Manage.*, 1997, **14**(5), 505–511.

14 K. Burashid and A. R. Hussain, Seawater RO plant operation and maintenance experience: Addur desalination plant operation assessment, *Desalination*, 2004, **165**, 11–22.
15 A State of Water Strategy for WA, Government of Western Australia, 2003, http://dows.lincdigital.com.au/files/State_Water_-Strategy_complete_001.pdf.
16 G. Srikanth, Membrane separation processes—technology and business opportunities, *Chem. Eng. World*, 1999, **34**(5), 55–66.
17 California Coastal Commission, *Seawater Desalination in California*, University of California Press, 2003.
18 D. V. Gauwbergen and J. Baeyens, Modeling and scaleup of reverse osmosis separation, *Environ. Eng. Sci.*, 2002, **19**(1), 37–45.
19 J. G. Wijmans and R. W. Baker, The solution–diffusion model: A review, *J. Membr. Sci.*, 1995, **107**, 1–21.
20 T. Hoepner, A procedure for environmental impact assessments (EIA) for seawater desalination plants, *Desalination*, 1999, **124**, 1–12.
21 S. E. Pantell, *Seawater desalination in California*, California Coastal Commission, 1993.
22 W. R. Everest and T. Murphree, Desalting residuals: A problem or a beneficial resource?, *Desalination*, 1995, **102**(1), 107–117.
23 J. V. Benne, D. G. Jirka and J. Largier, Ocean brine disposal, *Desalination*, 1994, **97**, 365–372.
24 M. C. Mickley, *Major ion toxicity in membrane concentrates*, AWWA Research foundation project No. 290, 2001.
25 G. L. Meerganz von Medeazza, Direct and socially-induced environmental impacts of desalination, *Desalination*, 2005, **185**, 57–70.
26 R. Einav, K. Harussi and D. Perry, The footprint of the desalination processes on the environment, *Desalination*, 2002, **152**, 141–154.
27 American Water Works Association, *Reverse Osmosis and Nanofiltration*, AWWA, M46, 173, 1999.
28 T. Hoepner and S. Lattemann, Chemical impacts from seawater desalination plants—a case study of the northern Red Sea, *Desalination*, 2002, **152**, 133–140.
29 B. Shi, W. Weizhong Xiao, S. James and J. S. Taylor, Influences of water treatment process on iron and copper release in distribution system, *J. Environ. Sci. Health*, 2006, **41**(8), 1667–1683.
30 J. Truesdall, M. Mickley and R. Hamilton, Survey of membrane drinking water plant disposal methods, *Desalination*, 1995, **102**, 93–105.
31 J. K. Kimes, The regulation of concentrate disposal in Florida, *Desalination*, 1995, **102**, 87–92.
32 A. Benzaoui and A. Bouabdallah, Desalination and biological wastewater treatment process, *Desalination*, 2004, **165**, 105–110.
33 T. Younos, The economics of desalination, *J. Contemp. Water Res. Educ.*, 2005, **132**, 39–45.

Mercury concentrations in coastal California precipitation: Evidence of local and trans-Pacific fluxes of mercury to North America

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[1] Because of mercury's (Hg) relatively high vapor pressure and long (0.5–2 years) atmospheric residence, there is the potential for long-range transport of contaminant Hg. Many studies have focused on that transport and deposition in central and eastern North America, Europe, and the Arctic, but there has been little research on the cycling of Hg in the western coast of North America. That deficiency is addressed in this preliminary study, which indicates there is long-range transport of Hg across the North Pacific. This transport is evidenced by the elevated (relative to equatorial and theoretical baseline) Hg concentrations in rainwater collected on the coast of California, as well as by the positive correlation between North Pacific storm tracks and Hg concentrations, with maximum concentrations associated with storms from 20°–40° latitude. Those tracks trace air masses containing industrial emissions with peak O_3 concentrations moving eastward off the Asian continent. The Asian fluxes appear to enhance Hg concentrations both directly, through the emission of particle-bound Hg and reactive Hg^{2+}, and indirectly, by increasing the rate of oxidation of Hg^0 in the atmosphere. Superimposed on the trans-Pacific background of industrial Hg is a local signal, with elevated concentrations at the urban site relative to the more pristine coastal site in California. This secondary enrichment is tentatively attributed to elevated local emissions of redox species, including O_3 and its precursors, which increase oxidation rates of Hg^0 in the atmosphere and Hg concentrations in precipitation. *INDEX TERMS:* 0365 Atmospheric Composition and Structure: Troposphere—composition and chemistry; 0368 Atmospheric Composition and Structure: Troposphere—constituent transport and chemistry; 0345 Atmospheric Composition and Structure: Pollution—urban and regional (0305); *KEYWORDS:* Mercury, atmosphere, oxidation, precipitation, transport, concentrations

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1. Introduction

[2] A large body of evidence has accumulated to support the hypothesis that, due to the relatively long residence time (0.5–2 years) of Hg^0 in the atmosphere [*Lamborg et al.*, 2000; *Lindqvist and Rodhe*, 1985; *Mason et al.*, 1994; *Seiler et al.*, 1980; *Slemr et al.*, 1985], Hg contamination is pandemic [*Fitzgerald et al.*, 1998; *Hudson et al.*, 1995; *Lindqvist et al.*, 1991; *Petersen et al.*, 1995]. The contamination is attributed to the oxidation of Hg^0 from the atmosphere to reactive species (e.g., Hg^{2+}) that are rapidly scavenged by settling particles and rain washout [*Lamborg et al.*, 2000; *Lin and Pehkonen*, 1999; *Munthe*, 1992; *Pleijel and Munthe*, 1995]. Those labile species are then readily available for biologically mediated methylation and accumulation in terrestrial and aquatic food chains [*Fitzgerald et al.*, 1998; *Lamborg et al.*, 1999; *Mason et al.*, 1997a; *Schroeder and Munthe*, 1998].

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[3] Recognition of the long-range atmospheric transport and transformation of Hg has coincided with an increased interest in the influence of atmospheric emissions from industrialized Asian countries on the environment. Asia has been identified as the major source of atmospherically deposited metals to the North Pacific [*Merrill*, 1989], and recent studies have evidenced the transport of Asian dust and industrial contaminants across the Pacific to western North America [*Berntsen et al.*, 1999; *Husar et al.*, 2001; *Jaffe et al.*, 1999]. In addition, coal combustion in China accounts for roughly 10% of the total industrial emissions of Hg [*Wang et al.*, 2000]. Consequently, this study was initiated to investigate the influence of Asian industrial emissions on Hg deposition rates in western North America.

2. Methods

[4] Rainwater samples were collected at two sites in central California (Figure 1). One was located on the coast at the University of California Santa Cruz's (UCSC) Long Marine Laboratory (LML), and the other was at Moffett

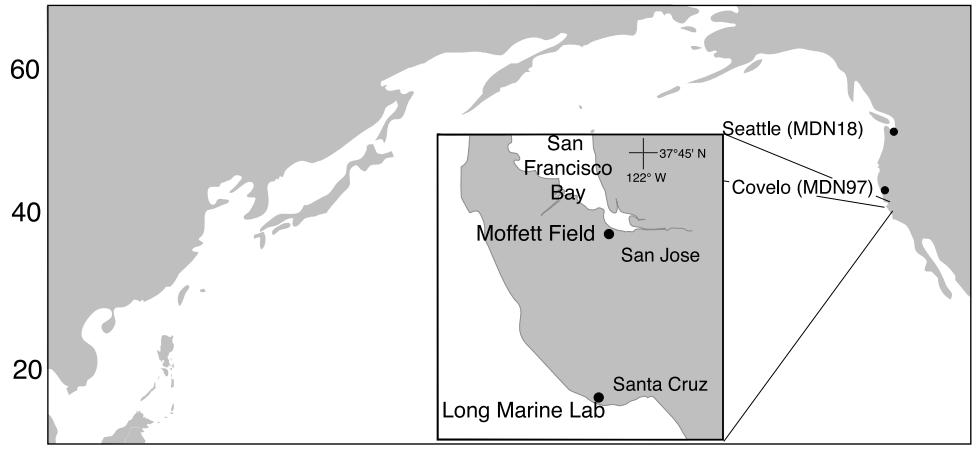

Figure 1. Location of sampling sites (inset) and MDN sites at Covelo, California, and Seattle, Washington.

Field (MF), on the other side (~50 km) of California's coastal range in the southern part of the San Francisco-San Jose-Oakland megalopolis. The coastal site (LML) was chosen to quantify the background concentration of Hg in storms directly off the Pacific, and the more inland site (MF) was chosen to investigate the impacts of local urbanization on Hg concentrations in rainwater. For reference, we compared our results at the two sites to those from two west coast Mercury Deposition Network (MDN) sites, which are located in Covelo (MDN97), California, and Seattle (MDN18), Washington (Figure 1).

[5] Collections were made using modified Aerochem Metrics 301 automated precipitation collectors, glass funnels, and Teflon™ receiving bottles using established methods, with trace metal clean techniques and high-purity reagents [*Dvonch et al.*, 1995; *Mason et al.*, 1992; *Mason et al.*, 1997b]. All sample handling and preparation was done in a HEPA filtered air (Class 100), trace metal clean room. The funnels and bottles were thoroughly cleaned in Trace Metal Grade (TMG, Fisher) acids (8N HNO_3 and 6N HCl) and rinsed (5 times) with Milli-Q (18 MΩ cm) water prior to deployment. Between events, the funnels and receiving bottles were rinsed 5 times with high-purity water, soaked in TMG 1.2N HCl, and then rinsed (5 times) before the next deployment.

[6] Immediately after an event, samples were returned to the lab, subdivided, and frozen prior to Hg analysis. Total Hg was measured after oxidation with 0.5 mL of 0.2 M BrCl using cold vapor atomic fluorescence spectroscopy, using established methods [*Bloom and Crecelius*, 1983; *Bloom and Fitzgerald*, 1988]. Method blanks averaged 10±5 pg, and the detection limit was 0.75 pM for a 100 mL sample.

[7] Aluminum was quantified by high-resolution inductively coupled plasma mass spectrometry (Finnegan Element 1). The analysis followed a HF/HNO_3/HCl (Seastar quartz distilled acids) digestion of 20 mL of sample, which was acidified with 0.5ml 12N HCl prior to digestion. This sample was dried down, digested with 1 mL 14N HF, then dried and digested with 1 mL 18N HNO_3 followed by 1 mL 12N HCl.

[8] Joyce Harris of the Climate Monitoring and Diagnostics Laboratory (CMDL) in Boulder, Colorado, provided air mass trajectory calculations. The calculations were performed using the CMDL isentropic model [*Harris and Kahl*, 1994], with 4 km arrival height for each event. The model was run to provide trajectory data for 10 days prior to each event.

3. Results and Discussion

3.1. Mercury Concentrations in Rain at Long Marine Lab

[9] Concentrations of Hg measured in rain at LML varied from 4–84 pM, with a volume weighted average of 30 pM (Figure 2). The range of concentrations are similar to that measured in the North Pacific (14–85 pM), but are elevated relative to concentrations measured in the equatorial Pacific (6.5–22.5 pM) [*Mason et al.*, 1992]. The volume-weighted concentration at LML was also similar to those (average = 28 pM) measured at the MDN97 in Covelo, California [*NADP*, 2001].

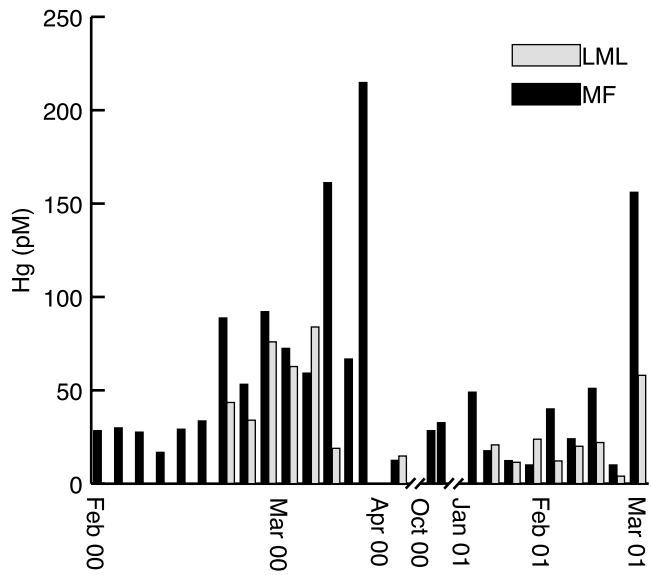

Figure 2. Concentration of Hg (pM) in rainwater at Moffett Field and Long Marine Lab.

Table 1. A Comparison Between Events at Moffett Field and Long Marine Lab[a]

	Moffett Field		Long Marine Lab	
Event Date	Hg, pM	Rainfall, mm	Hg, pM	Rainfall, mm
30 January 2000	28.38	1.51		
3 February 2000	29.89	4.26		
10 February 2000	27.61	2.73		
12 February 2000	16.78	18.73		
14 February 2000	29.17	22.07		
20 February 2000	33.60	10.10		
23 February 2000	88.74	22.58	43.35	1.82
24 February 2000	53.23	1.55	34.00	1.74
27 February 2000	92.13	9.03	76.09	10.95
28 February 2000	72.47	6.76	62.74	9.08
2 March 2000	59.21	1.95	151.54	0.45
5 March 2000	161.20	11.73	83.92	25.97
9 March 2000	66.76	13.92	18.94	13.30
10 March 2000	214.82	6.32		
14 April 2000	12.31	7.22	14.78	19.59
28 October 2000	28.07	8.41		
30 October 2000	32.30	25.16		
14 January 2001	49.11	24.87		
24 January 2001	17.60	3.56	20.74	16.18
25 January 2001	12.31	12.86	11.42	8.21
29 January 2001	9.92	1.12	23.78	1.37
11 February 2001	40.08	28.19	12.36	15.61
18 February 2001	24.28	4.64	19.59	12.09
22 February 2001	50.85	24.71	21.94	3.02
25 February 2001	10.22	4.76	4.04	28.32
2 March 2001	156.04	5.95	58.08	5.59
3 March 2001			22.78	26.66

[a]The RSD on the Hg concentration measurements is ±10%, as determined by duplicate analyses of samples.

[10] Since that latter site is in a very rural location along the California coast, its Hg concentrations are considered to represent the background concentration of Hg in rainwater on the west coast of North America. The similarity between the MDN97 Covelo site and LML substantiates the proposal that Hg concentrations at LML also approach background concentrations, although there is the possibility that some of the Hg at LML is from local emissions.

3.2. Mercury Concentrations in Rain at Moffett Field

[11] Mercury concentrations measured at MF ranged from 4–214 pM and averaged 58 pM, (Figure 2). By comparison, integrated two-week samples collected concurrently at the MF site, at MDN72, averaged 48 pM [*Tsai and Hoenicke*, 2001]. Since other sites in San Francisco Bay have reported averages of 32–36 pM [*Tsai and Hoenicke*, 2001], the marginally higher concentrations observed at MF are tentatively attributed to its downwind location from areas of industrialization and urbanization within the Bay area. The concentrations from MF also compare well to those in samples collected at MDN18 in Seattle, where the long-term (3 years) average is 53 pM [*National Atmospheric Deposition Program*, 2001]. In contrast, the maximum Hg concentrations at all of the west coast sites (MDN18, MDN97, LML, MF) are lower than maximums (~400 pM) observed at the east coast of the United States [*Mason et al.*, 1997b].

3.3. Enrichment in Hg Concentrations at MF Relative to LML

[12] A simple linear, regression analysis comparing MF and LML indicates a highly significant (P = 0.006, paired t-test), 44% enrichment in the Hg concentration of individual rain events at MF compared to LML (Figure 2). Since there is less rainfall at MF than at LML, these higher concentrations might be due to lower dilution of individual events. However, the enrichment is present at MF regardless of relative rainfall at each site (Table 1).

[13] The enrichment, therefore, is tentatively attributed to a combination of factors related to urban activity. These include higher soot particle concentrations, which effectively scavenge reactive mercury species; higher ozone concentrations, which increase atmospheric Hg^0 oxidation rates; and greater local emissions of natural and industrial Hg, from cinnabar deposits and diverse anthropogenic activities in the San Francisco Bay area, respectively.

[14] Another possible explanation for the enrichment at MF is its proximity to San Francisco Bay. Moffett Field, located in the Bay's wetlands, may be influenced by natural processes, which are similar to those observed in oceanic environments [*Mason*, 2001; *Schroeder et al.*, 1998]. Specifically, the influence of Bay surface waters may result in higher Hg deposition rates through boundary layer recycling of Hg^0, which has been hypothesized to react with Cl and Br gas, allowing for local deposition of oxidized Hg [*Mason*, 2001]. This potential source of enrichment, however, does not account for the variability seen in Hg concentrations at both sites, because the consistent magnitude of this enrichment suggests that it is superimposed on another, nonlocal, mechanism, which is governing Hg concentrations in rain on the West Coast.

3.4. Depositional Fluxes

[15] While volume weighted concentrations of Hg in rainwater are lower at LML (30 pM) relative to MF (58 pM), the annual wet deposition at LML (20 nmol m^{-2} yr^{-1}) and MF (22 nmol m^2 yr^{-1}) are similar (Table 2). The similarity is primarily due to the higher amount of rainfall at LML, which is consistent with the relationship between flux and rainfall observed in both terrestrial [*Mason et al.*, 1997a] and open ocean [*Lamborg et al.*, 1999] environments.

[16] The Hg:^{210}Pb correlation in rainwater recently observed in Wisconsin [*Lamborg et al.*, 2000] and the Atlantic Ocean [*Lamborg et al.*, 1999] has been used to calculate Hg deposition using known ^{210}Pb deposition rates [*Lamborg et al.*, 2000]. We have tested the validity of this model at our sites using (1) the ^{210}Pb deposition estimates [*Turekian*, 1977] for the west coast of North America and (2) the slope of the proposed global Hg:^{210}Pb relationship (0.06 ng*m Bq^{-1}). The resultant ratio indicates an annual Hg deposition rate of 25–50 nmol m^{-2} yr^{-1} in this coastal region, comparable with our independent calculations based on measured Hg concentrations in rainwater (Table 2).

[17] Finally, the total pre-industrial flux of Hg to the world's oceans is estimated at 3 Mmol/yr [*Mason et al.*, 1994], which averages 8.3 nmol/m^2/yr [*Mason et al.*, 1994]. Assuming that the pre-industrial flux at LML is comparable to that in the open ocean, the modern value is about twofold to threefold enriched relative to the pre-industrial flux estimate. While there are numerous limitations to this estimate, the twofold to threefold increase in deposition of Hg at LML, compares well to other estimates of the magnitude of the increase (~3 times) of Hg deposition

Table 2. Deposition Estimates of Hg at Long Marine Lab and Moffett Field[a]

Site	Volume Weighted Average Hg Concentration, pM	Annual Average Rainfall, cm	Deposition, μmol/m^2/yr
Moffett Field	58	35	22
Long Marine Lab	30	74	20

[a]Estimates are based on the data collected during the study period, and should be considered representative for that period. A longer study period is necessary to generate long term wet deposition estimates, and to quantify the annual variability in that deposition. In addition, roughly 80% of the events during the study period were sampled at MF and roughly 70% at LML. As a result, there is the potential that the volume-weighted averages used in these calculations are biased by the exclusion of extremely low- or high-concentration events. However, as our data at MF compares well to independent measurements made at MF during the same period as part of the MDN, we do not believe that these estimates are biased.

globally as a result of anthropogenic activities [*Mason et al.*, 1994].

3.5. Enrichment Factors

[18] To assess the relative contribution of natural Hg in crustal material, enrichment factors [*Duce et al.*, 1991] were calculated using published crustal concentrations [*Mason and Moore*, 1982; *Taylor*, 1964]. The enrichment factors, which ranged from 900–5700 at both sites, are much higher than those (4–40) reported in Atlantic rainwater, [*Lamborg et al.*, 1999]. The factors calculated for the Atlantic, however, involved samples with a large component of Saharan dust with a very low Hg/Al ratio that diluted the atmospheric signal.

[19] The relatively high enrichment factors at LML and MF do not necessarily imply enrichment from local anthropogenic fluxes of Hg, as the contribution from industrial emissions and natural oxidation would be difficult to tell apart using enrichment factors alone. The high enrichment factors do indicate that Hg in rainwater is not primarily derived from terrestrial dust. They are also indicative of an atmospheric source of Hg^{2+} to rainwater, which is consistent with the accepted models of Hg cycling in the atmosphere [*Lamborg et al.*, 2000; *Lin and Pehkonen*, 1999; *Munthe and McElroy*, 1992; *Pleijel and Munthe*, 1995].

3.6. Sources of Hg in the North Pacific

[20] In the Pacific basin, the dominant anthropogenic source of Hg to the atmosphere is coal combustion in China, an annual flux of 1.5 Mmol of Hg to the atmosphere [*Wang et al.*, 2000]. For comparison, this flux is double the estimated total anthropogenic Hg emissions (0.78 Mmol/yr) in the United States [*USEPA*, 1997], and accounts for roughly 10% of global industrial emissions (16.5–22 Mmol/yr) [*Mason et al.*, 1994]. With a 0.5–2 year residence time in the atmosphere, Hg^0 emissions from Chinese coal combustion are distributed on a global scale. However, emissions from coal combustion occur in both the vapor (Hg^0) and reactive Hg^{2+} states, and the reactive proportion is likely scavenged and deposited in Asia and the Pacific basin.

[21] Contrasted to anthropogenic emissions, natural emissions in the North Pacific are relatively minor, with the two dominant natural sources of Hg^0 being evasion from surface waters and emissions from volcanoes. In the case of evasion from surface waters, the majority of emissions are the result of reduction of atmospherically deposited Hg^{2+} in surface waters [*Mason et al.*, 1994]. On a global scale, this deposition and resulting evasion is estimated to be enriched 3 times over pre-anthropogenic values; and, as a result, the majority of emissions from surface waters are assumed to have anthropogenic origins [*Mason et al.*, 1994]. While there are few estimates of emissions from volcanoes within the Pacific Basin, the available estimates suggest low emissions (e.g., 5.75 mol/yr, for Kilauea Volcano in Hawaii) relative to anthropogenic emissions in the Pacific basin [*Varekamp and Buseck*, 1986]. Similarly, global emission estimates from volcanic activity range from 0.1–0.45 Mmol/yr [*Fitzgerald*, 1996]. These emissions are minor relative to both total anthropogenic emissions, and the estimated Chinese emissions, especially considering only a fraction of these volcanic emissions occur in the Pacific Basin. Therefore, the majority of Hg^0 in the atmosphere, and the majority of that Hg^0 which is reduced and deposited to land and sea surfaces is anthropogenic in origin.

3.7. Washout of Particle-Bound Hg

[22] A local washout of particle-associated Hg is not seen at MF or LML, with relatively homogenous Hg concentrations over a highly variable precipitation (1–25 mm) event size (Figure 3). Washout of particle-bound Hg is interpreted to be the cause of the strong exponential decrease in Hg concentration with increasing rainfall as observed in both continental [*Mason et al.*, 1997b] and open ocean [*Lamborg et al.*, 1999] environments. The lack of an exponential decrease in concentration with increasing event size in our data suggests that primarily nonlocal processes control the observed variability in Hg concentrations.

[23] The hypothesis that nonlocal processes are the major control on the variability of the concentrations observed was assessed by calculating the particle concentrations required to produce the concentrations observed. This was done with determination of the scavenging ratio [*Duce et al.*, 1991], which defines a relationship between rainwater concentrations and atmospheric particle concentrations as

$$W = [Hg_{rain}]^{*}\rho/[Hg_{atm}],$$

where

W = Scavenging ratio
$[Hg_{rain}]$ = Concentration of Hg in rain
ρ = Density of atmosphere
$[Hg_{atm}]$ = Concentration of Hg in the atmosphere.

Reported scavenging ratios range from 300–600 in midcontinental regions [*Fitzgerald et al.*, 1994; *Lamborg et al.*, 1995], to 1100 on the east coast of the United States [*Mason et al.*, 1997b], and ~1300 in the equatorial Pacific [*Mason et al.*, 1992]. Using a range of 500 to 1000, the volume weighted average concentrations in rainfall could be explained by atmospheric Hg particle concentrations of 71–141 fmol/m^3 at MF and 52–105 fmol/m^3 at LML. These values compare to reported atmospheric Hg particle concentrations of 2–9 fmol/m^3 in the North Pacific [*Fitzgerald*, 1989], 12 fmol/m^3 in the Atlantic [*Lamborg et al.*, 1999] and ~100 fmol/m^3 in continental settings [*Dvonch et al.*, 1995; *Keeler et al.*, 1995; *Lamborg et al.*, 1995; *Mason et al.*, 1997b].

[24] Given the rural, coastal location of LML, and the direction of prevailing winds (from the northwest, off the

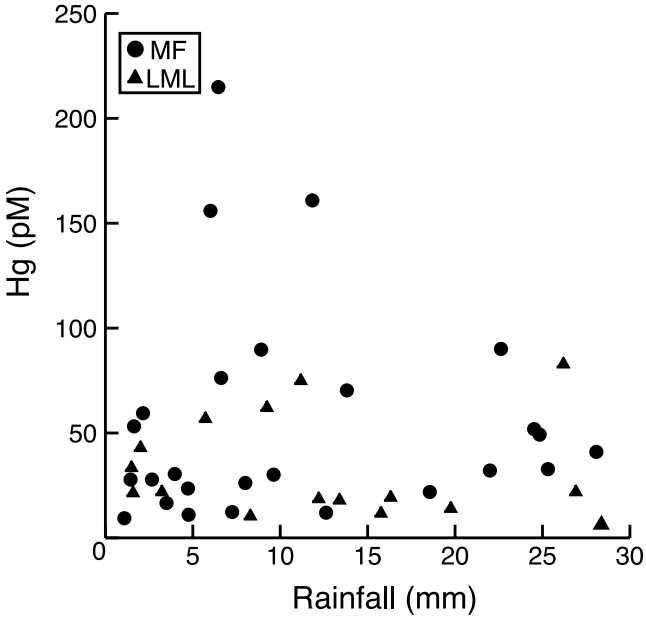

Figure 3. Total Hg versus rainfall for individual events at Long Marine Lab (triangles) and at Moffett Field (circles).

ocean) atmospheric Hg concentrations at LML are, as discussed above, assumed to be similar to those of open ocean sites. With this assumption, the particle concentration needed to account for the observed average rain concentrations is at least double that observed in open ocean environments. This disparity suggests that there is another source of Hg^{2+} to rainwater besides particle-bound Hg, which is consistent with an atmospheric source suggested by the high enrichment factors.

3.8. Air Mass Trajectory Calculations

[25] The preceding analyses indicate that a mechanism, other than local particle washout, is needed to explain the observed variability in rainwater Hg concentrations at both LML and MF. Trajectory calculations of air parcels associated with each event demonstrate a pattern of Hg concentration in rain, which is controlled by storm tracks across the North Pacific (Figure 4). Comparing the data in this study with samples from the North Pacific collected in the 1980s [*Fitzgerald*, 1989] and with equatorial samples collected in 1990 [*Mason et al.*, 1992] reveals a pattern of low Hg concentrations in rainwater in equatorial regions, higher concentrations in the midlatitudes, and slightly decreasing concentrations in the northern latitudes (Figure 4). This latitudinal pattern suggests that large-scale processes are involved in controlling the variability of Hg concentrations observed in this study. Most notably, the peak concentrations at middle latitudes suggest a source in Asia, which appears to influence Hg concentrations in rain on the coast of California.

3.9. Long-Range Sources of Hg

[26] Additional analyses of the sources of Hg in rain in the Pacific Basin are necessary in order assess the validity of the proposal that industrial emissions from Asia are the primary source of Hg in North Pacific rain. The dominant species of Hg in the atmosphere is Hg^0, but reactive Hg^{2+} has been demonstrated to be the dominant species of Hg in rainwater. Given the evidence for a nonlocal atmospheric source of Hg in precipitation, consideration of the atmospheric processes responsible for the generation of Hg^{2+} in the atmosphere is necessary in evaluating potential sources of Hg in rainwater.

[27] While our understanding of the atmospheric chemistry of Hg is far from complete, there are two current accepted processes by which Hg^0 is oxidized and incorpo-

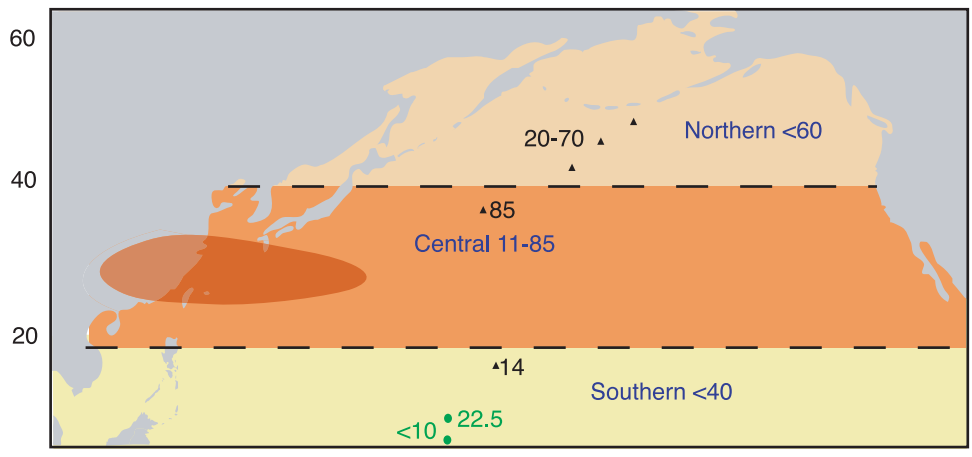

Figure 4. Relationship between storm tracks and Hg concentrations at Long Marine Lab. Storm tracks have been sorted into three categories, represented by dashed lines. Concentrations (pM) are given in blue for each category, with peak concentrations associated with the midlatitude storm tracks. For comparison, previous measurements of Hg in rainwater in the Pacific are given; circles are from *Mason et al.* [1992], triangles from SEAREX [*Fitzgerald*, 1989]. In addition, the area of maximum ozone production and export is plotted [*Mauzerall et al.*, 2000], which corresponds to the peak Hg concentrations observed in this study. See text for discussion.

rated in rainwater. One of these mechanisms, the Cloud Conversion Model (CCM), proposed by Pleijel and Munthe [*Munthe and McElroy*, 1992; *Pleijel and Munthe*, 1995], focuses on the oxidation of Hg^0 in the aqueous phase, and then scavenging of the reactive Hg by soot contained in raindrops. The other mechanism suggests the production of Hg^{2+} in the gas phase (reaction of Hg^0 with either O_3 or H_2O_2) may be the dominant mechanism [*Lamborg et al.*, 2000].

[28] Other models [*Bergan and Rodhe*, 2001] have built on this work, and suggest that the kinetics of O_3 oxidation of Hg^0 is too slow to explain the observed trends in atmospheric Hg speciation and distribution. Work on depletion of Hg^0 during polar sunrise in the Arctic has shown a positive correlation with O_3 [*Schroeder et al.*, 1998], which is attributed to the generation of free halogen species, highly effective oxidizers of Hg^0 [*Schroeder and Munthe*, 1998], during the photodegradation of O_3 [*Lu et al.*, 2001]. The production of halogen species has also been demonstrated to occur during O_3 degradation at lower latitudes [*Dickerson et al.*, 1999], and these halogen species are thought to play an important part in the oxidation of Hg^0 in the marine boundary layer [*Mason*, 2001]. As a result, the oxidation of Hg^0 in the marine environment will be strongly influenced by the concentration of O_3, either directly, through oxidation of Hg^0 or indirectly through the production of reactive halogen species as that O_3 photodegrades.

[29] Asia, and in particular, China, has received a great deal of scientific attention recently as a result of increasing impacts on atmospheric O_3 concentrations due to industrial activities [*Carmichael et al.*, 1998; *Mauzerall et al.*, 2000; *Pochanart et al.*, 1999]. During wintertime, there is a maximum in O_3 production in China as a result of biomass burning, coal combustion and other industrial activities, and, coupled with strong northwesterly continental outflow, these activities result in maximum O_3 concentrations in the western Pacific [*Mauzerall et al.*, 2000]. This O_3 is available for oxidation of ambient Hg^0 through the mechanisms described above, and, if the resulting reactive Hg^{2+} is incorporated in developing storms, it will be effectively transported across the Pacific to the west coast of North America as indicated in Figure 4.

[30] Therefore, O_3 should be considered a tracer for potential oxidation of Hg^0, through both direct and indirect oxidation of Hg^0. The elevated Hg concentrations in rain observed in this study, then, are most likely the result of Asian emissions of both Hg and O_3 and its precursors, although the later may play a more important role in supplying Hg^{2+} to rainwater. These emissions will combine to enhance Hg^0 oxidation rates in the Pacific basin, ultimately resulting in elevated Hg concentrations in rainwater sourced within the basin. This phenomenon has been used to explain Hg deposition in Florida, where recent work suggests that up to 80% of deposition to the Florida Everglades is the result of production of reactive Hg^{2+} species in the marine boundary layer that is then scavenged and deposited by storms in Florida [*Guentzel et al.*, 2001].

4. Conclusions

[31] This initial study demonstrates the impact of Asian industrial emissions on Hg concentrations in rain in western North America. The analyses substantiate previous reports on the influence of those emissions on Hg deposition in the North Pacific, first proposed by Bill Fitzgerald and his colleagues during the SEAREX program [*Fitzgerald*, 1989]. The increased Hg concentrations in rainwater in central California are attributed to a series of atmospheric reactions, and are not dependent solely on emissions of industrial Hg to the atmosphere. Rather, the concentrations may be due to a combination of particle-bound Hg emissions from Asia and a series of redox reactions centered around the destruction of O_3 in the marine troposphere, that increases production of atmospheric Hg^{2+} above background levels. Rainwater, contained in storms forming in the Western Pacific, then transports this contaminant Hg across the Pacific to the west coast of North America.

[32] Superimposed on this long-range transport of Hg in storms are local inputs due to human activities. Those inputs are evidenced by the 44% enrichment of Hg concentrations in precipitation at the urban site (MF) relative to the coastal site (LML). The enrichment could be the result of local industrial Hg emissions, soot, or redox species emissions, which result in higher concentrations of Hg in rainwater at MF relative to LML. Alternatively, the enrichment may be the result of higher O_3 concentrations, which will facilitate direct and indirect oxidation of Hg^0. Additionally, San Francisco Bay, which abuts MF, may supply the sea salt aerosols necessary to generate free halogens during O_3 degradation.

[33] Both of these apparently local and trans-Pacific fluxes demonstrate the increasing importance in understanding the atmospheric chemistry of Hg. Our understanding of the sources of Hg deposited to terrestrial and aquatic environments is directly linked to our understanding of the redox reactions governing the production of Hg^{2+} in the atmosphere, and here we demonstrate how the influence of anthropogenic emissions impact Hg on both regional and hemispheric scales. These data corroborate other recent reports that indicate efforts to regulate Hg concentrations in fish and waterways must focus not only on Hg emissions, but also on emissions of redox species such as O_3 if they are to achieve their desired reductions in concentrations.

[34] **Acknowledgments.** The authors are grateful for the assistance of Pam Tsai at the San Francisco Estuary Institute, Eric Hansen at the City of San Jose, and Kobin Lee, with NASA, at Moffett Field. Rob Mason and his lab at the University of Maryland's Chesapeake Biological Laboratory offered invaluable technical and scientific advice. Joyce Harris and the Climate Monitoring and Diagnostics Laboratory (CMDL) in Boulder, Colorado, provided the trajectory calculations. This study was funded in part by grants from the University of California's Toxic Substances Research and Teaching Program, the San Francisco Estuary Institute's Regional Monitoring Program for Toxic Substances, and the W. M. Keck Foundation.

References

Bergan, T., and H. Rodhe, Oxidation of elemental mercury in the atmosphere: Constraints imposed by global scale modelling, *J. Atmos. Chem.*, *40*(2), 191–212, 2001.

Berntsen, T. K., S. Karlsdottir, and D. A. Jaffe, Influence of Asian emissions on the composition of air reaching the North Western United States, *Geophys. Res. Lett.*, *26*(14), 2171–2174, 1999.

Bloom, N. S., and E. A. Crecelius, Determination of mercury in seawater at sub-nanogram per liter levels, *Marine Chem.*, *14*, 49–59, 1983.

Bloom, N. S., and W. F. Fitzgerald, Determination of volatile species at the picogram level by low temperature gas chromatography with cold vapor atomic fluorescence detection, *Anal. Chim. Acta*, *208*, 151–161, 1988.

Carmichael, G. R., I. Uno, M. J. Phadnis, Y. Zhang, and Y. Sunwoo, Tropospheric ozone production and transport in the springtime in east Asia, *J. Geophys. Res.*, *103*(D9), 10,649–10,671, 1998.

Dickerson, R. R., K. P. Rhoads, T. P. Carsey, S. J. Oltmans, J. P. Burrows, and P. J. Crutzen, Ozone in the remote marine boundary layer: A possible role for halogens, *J. Geophys. Res.*, *104*(D17), 21,385–21,395, 1999.

Duce, R. A., et al., The atmospheric input of trace species to the world ocean, *Global Biogeochem. Cycles*, *5*(3), 193–259, 1991.

Dvonch, J. T., A. F. Vette, G. J. Keeler, G. Evans, and R. Stevens, An Intensive Multi-Site Pilot Study Investigating Atmospheric Mercury in Broward County, *Florida, Water Air Soil Pollut.*, *80*(1–4), 169–178, 1995.

Fitzgerald, W. F., Atmospheric and Oceanic Cycling of Mercury, in *SEAREX: The Sea/Air Exchange Program*, edited by R. A. Duce, J. P. Riley, and R. Chester, pp. 152–180, Academic, New York, 1989.

Fitzgerald, W. F., Mercury emissions from volcanoes, in *4th International Conference on Mercury as a Global Pollutant*, edited by R. Ebinghaus, G. Peterson, and U. V. Tumpling, p. 87, Hamburg, 1996.

Fitzgerald, W. F., G. M. Vandal, R. P. Mason, and F. Dulac, Air-water cycling of mercury in lakes, in *Mercury Pollution, Integration and Synthesis*, edited by C. J. Watras and J. W. Huckabee, pp. 203–220, Lewis Publishers, Ann Arbor, Mich., 1994.

Fitzgerald, W. F., D. R. Engstrom, R. P. Mason, and E. A. Nater, The case for atmospheric mercury contamination in remote areas, *Environ. Sci. Technol.*, *32*(1), 1–7, 1998.

Guentzel, J. L., W. M. Landing, G. A. Gill, and C. D. Pollman, Processes influencing rainfall deposition of mercury in Florida, *Environ. Sci. Technol.*, *35*(5), 863–873, 2001.

Harris, J. M., and J. D. W. Kahl, Analysis of 10-day isentropic flow patterns for Barrow, Alaska: 1985–1992, *J. Geophys. Res.*, *99*(D12), 25,845–25,855, 1994.

Hudson, R. J. M., S. A. Gherini, W. F. Fitzgerald, and D. B. Porcella, Anthropogenic Influences On the Global Mercury Cycle: A Model-Based Analysis, *Water Air Soil Pollut.*, *80*(1–4), 265–272, 1995.

Husar, R. B., et al., Asian dust events of April 1998, *J. Geophys. Res.*, *106*(D16), 18,317–18,330, 2001.

Jaffe, D., et al., Transport of Asian air pollution to North America, *Geophys. Res. Lett.*, *26*(6), 711–714, 1999.

Keeler, G., G. Glinsorn, and N. Pirrone, Particulate Mercury in the Atmosphere: Its Significance, Transport, Transformation and Sources, *Water Air Soil Pollut.*, *80*(1–4), 159–168, 1995.

Lamborg, C. H., W. F. Fitzgerald, W. C. Graustein, and K. K. Turekian, An examination of the atmospheric chemistry of mercury using Pb-210 and Be-7, *J. Atmos. Chem.*, *36*(3), 325–338, 2000.

Lamborg, C. H., W. F. Fitzgerald, G. M. Vandal, and K. R. Rolfhus, Atmospheric Mercury in Northern Wisconsin - Sources and Species, *Water Air Soil Pollut.*, *80*(1–4), 189–198, 1995.

Lamborg, C. H., K. R. Rolfhus, W. F. Fitzgerald, and G. Kim, The atmospheric cycling and air-sea exchange of mercury species in the South and equatorial Atlantic Ocean, *Deep Sea Res., Part II*, *46*(5), 957–977, 1999.

Lin, C. J., and S. O. Pehkonen, The chemistry of atmospheric mercury: A review, *Atmos. Environ.*, *33*(13), 2067–2079, 1999.

Lindqvist, O., K. Johansson, M. Aastrup, A. Andersson, L. Bringmark, G. Hovsenius, L. Hakanson, A. Iverfeldt, M. Meili, and B. Timm, Mercury in the Swedish Environment: Recent Research On Causes, Consequences and Corrective Methods, *Water Air Soil Pollut.*, *55*(1–2), R11+, 1991.

Lindqvist, O., and H. Rodhe, Atmospheric mercury: A review, *Tellus*, *37B*, 136–159, 1985.

Lu, J. Y., W. H. Schroeder, L. A. Barrie, A. Steffen, H. E. Welch, K. Martin, L. Lockhart, R. V. Hunt, G. Boila, and A. Richter, Magnification of atmospheric mercury deposition to polar regions in springtime: The link to tropospheric ozone depletion chemistry, *Geophys. Res. Lett.*, *28*(17), 3219–3222, 2001.

Mason, B., and C. B. Moore, *Principles of Geochemistry*, John Wiley, New York], 1982.

Mason R. P., The role of atmospheric chemistry and the air-water exchange in the global mercury cycle, in *6th International Conference on Mercury as a Global Pollutant*, Minamata, Japan, 2001.

Mason, R. P., W. F. Fitzgerald, and F. M. M. Morel, The Biogeochemical Cycling of Elemental Mercury: Anthropogenic Influences, *Geochim. Cosmochim. Acta*, *58*(15), 3191–3198, 1994.

Mason, R. P., W. F. Fitzgerald, and G. M. Vandal, The Sources and Composition of Mercury in Pacific Ocean Rain, *J. Atmos. Chem.*, *14*(1–4), 489–500, 1992.

Mason, R. P., N. M. Lawson, and K. A. Sullivan, Atmospheric deposition to the Chesapeake Bay watershed: Regional and local sources, *Atmos. Environ.*, *31*(21), 3531–3540, 1997a.

Mason, R. P., N. M. Lawson, and K. A. Sullivan, The concentration, speciation and sources of mercury in Chesapeake Bay precipitation, *Atmos. Environ.*, *31*(21), 3541–3550, 1997b.

Mauzerall, D. L., D. Narita, H. Akimoto, L. Horowitz, S. Walters, D. A. Hauglustaine, and G. Brasseur, Seasonal characteristics of tropospheric ozone production and mixing ratios over East Asia: A global three-dimensional chemical transport model analysis, *J. Geophys. Res.*, *105*(D14), 17,895–17,910, 2000.

Merrill, J. T., Atmospheric Long-range Transport to the Pacific Ocean, in *SEAREX: The Sea/Air Exchange Program*, edited by R. A. Duce, J. P. Riley, and R. Chester, pp. 15–49, Academic, New York, 1989.

Munthe, J., The Aqueous Oxidation of Elemental Mercury By Ozone, *Atmos. Environ., Part A*, *26*(8), 1461–1468, 1992.

Munthe, J., and W. J. McElroy, Some Aqueous Reactions of Potential Importance in the Atmospheric Chemistry of Mercury, *Atmos. Environ., Part A*, *26*(4), 553–557, 1992.

NADP, National Atmospheric Deposition Program (NRSP-3)/Mercury Deposition Network, NADP Program Office, Illinois State Water Survey, Champaign, Ill., 2001.

Petersen, G., A. Iverfeldt, and J. Munthe, Atmospheric Mercury Species Over Central and Northern Europe: Model Calculations and Comparison With Observations From the Nordic Air and Precipitation Network For 1987 and 1988, *Atmos. Environ.*, *29*(1), 47–67, 1995.

Pleijel, K., and J. Munthe, Modelling the Atmospheric Mercury Cycle: Chemistry in Fog Droplets, *Atmos. Environ.*, *29*(12), 1441–1457, 1995.

Pochanart, P., J. Hirokawa, Y. Kajii, H. Akimoto, and M. Nakao, Influence of regional-scale anthropogenic activity in northeast Asia on seasonal variations of surface ozone and carbon monoxide observed at Oki, *Japan, J. Geophys. Res.*, *104*(D3), 3621–3631, 1999.

Schroeder, W. H., K. G. Anlauf, L. A. Barrie, J. Y. Lu, A. Steffen, D. R. Schneeberger, and T. Berg, Arctic springtime depletion of mercury, *Nature*, *394*(6691), 331–332, 1998.

Schroeder, W. H., and J. Munthe, Atmospheric mercury: An overview, *Atmos. Environ.*, *32*(5), 809–822, 1998.

Seiler, W., C. Eberling, and F. Slemr, Global distribution of gaseous mercury in the troposphere, *Pure Appl. Geophys.*, *118*, 963–973, 1980.

Slemr, F., G. Schuster, and W. Seiler, Distribution, speciation, and budget of atmospheric mercury, *J. Atmos. Chem.*, *3*, 407–434, 1985.

Taylor, S. R., Abundance of chemical elements in the continental crust: A new table, *Geochem. Cosmochem. Acta*, *28*, 1273–1285, 1964.

Tsai, P., and R. Hoenicke, San Francisco Bay Atmospheric Deposition Pilot Study, Mercury, p.18, San Francisco Estuary Instit., Richmond, Calif., 2001.

Turekian, K. K., The fate of metals in the oceans, *Geochim. Cosmochim. Acta*, *41*(8), 1139–1144, 1977.

USEPA, Office of Research and Development, *Mercury study report to Congress*, Office of Air Quality Planning and Standards and Office of Research and Development, U.S. Environmental Protection Agency, Research Triangle Park, N.C., 1997.

Varekamp, J. C., and P. R. Buseck, Global mercury flux from volcanic and geothermal sources, *Applied Geochem.*, *1*, 65–73, 1986.

Wang, Q., W. G. Shen, and Z. W. Ma, Estimation of mercury emission from coal combustion in China, *Environ. Sci. Technol.*, *34*(13), 2711–2713, 2000.

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Treatment Technology Review and Assessment

Association of Washington Business
Association of Washington Cities
Washington State Association of Counties

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Acronyms

Acronym	Definition
AACE	Association for the Advancement of Cost Engineering
AOP	advanced oxidation processes
AWB	Association of Washington Businesses
BAC	biological activated carbon
BAP	benzo(a)pyrene
BOD	biochemical oxygen demand
BTU	British thermal unit
CEPT	Chemically-enhanced primary treatment
cf	cubic feet
CIP	clean in place
CRITFC	Columbia River Inter-Tribal Fish Commission
Ecology	Washington Department of Ecology
EPA	U.S. Environmental Protection Agency
FCR	fish consumption rate
g/day	grams per day
GAC	granular activated carbon
gal	gallon
gfd	gallons per square foot per day
GHG	greenhouse gas
gpd	gallons per day
gpm	gallons per minute
GWh	giga watt hours
HDR	HDR Engineering, Inc.
HHWQC	human health water quality criteria
HRT	hydraulic residence time
IPCC	Intergovernmental Panel on Climate Change
kg	kilogram
KWh/MG	kilowatt-hours per million gallons
lb	pound
MBR	membrane bioreactor
MCL	maximum contaminant level
MF	microfiltration
mgd	million gallons per day
mg/L	milligrams per liter
MMBTU	million British thermal units
MWh/d	megawatt-hours per day
NF	nanofiltration
ng/L	nanograms per liter
NPDES	National Pollutant Discharge Elimination System
NPV	net present value
O&M	operations and maintenance
ODEQ	Oregon Department of Environmental Quality
PAC	powdered activated carbon
PAH	polycyclic aromatic hydrocarbons
PCB	polychlorinated biphenyls
PE	population equivalents
PIX	potable ion exchange

Acronym	Definition
ppm	parts per million
RO	reverse osmosis
SDWA	Safe Drinking Water Act
sf	square feet
SGSP	salinity gradient solar pond
SRT	solids retention time
Study Partners	Association of Washington Businesses/Association of Washington Cities and Washington State Association of Counties consortium
TDS	total dissolved solids
TMDL	total maximum daily load
TSS	total suspended solids
UF	ultrafiltration
µg/L	micrograms per liter
USDA	U.S. Department of Agriculture
UV	ultraviolet
WAC	Washington Administrative Code
WAS	waste activated sludge
WLA	waste load allocation
WWTP	wastewater treatment plant
ZLD	zero liquid discharge

Executive Summary

This study evaluated treatment technologies potentially capable of meeting the State of Washington Department of Ecology's (Ecology) revised effluent discharge limits associated with revised human health water quality criteria (HHWQC). HDR Engineering, Inc. (HDR) completed a literature review of potential technologies and an engineering review of their capabilities to evaluate and screen treatment methods for meeting revised effluent limits for four constituents of concern: arsenic, benzo(a)pyrene (BAP), mercury, and polychlorinated biphenyls (PCBs). HDR selected two alternatives to compare against an assumed existing baseline secondary treatment system utilized by dischargers. These two alternatives included enhanced secondary treatment with membrane filtration/reverse osmosis (MF/RO) and enhanced secondary treatment with membrane filtration/granulated activated carbon (MF/GAC). HDR developed capital costs, operating costs, and a net present value (NPV) for each alternative, including the incremental cost to implement improvements for an existing secondary treatment facility.

Currently, there are no known facilities that treat to the HHWQC and anticipated effluent limits that are under consideration. Based on the literary review, research, and bench studies, the following conclusions can be made from this study:

- Revised HHWQC based on state of Oregon HHWQC (2001) and U.S. Environmental Protection Agency (EPA) "National Recommended Water Quality Criteria" will result in very low water quality criteria for toxic constituents.
- There are limited "proven" technologies available for dischargers to meet required effluent quality limits that would be derived from revised HHWQC.
    - Current secondary wastewater treatment facilities provide high degrees of removal for toxic constituents; however, they are not capable of compliance with water quality-based National Pollutant Discharge Elimination System (NPDES) permit effluent limits derived from the revised HHWQC.
    - Advanced treatment technologies have been investigated and candidate process trains have been conceptualized for toxics removal.
        - Advanced wastewater treatment technologies may enhance toxics removal rates; however, they will not be capable of compliance with HHWQC-based effluent limits for PCBs. The lowest levels achieved based on the literature review were between <0.00001 and 0.00004 micrograms per liter (µg/L), as compared to a HHWQC of 0.0000064 µg/L.
        - Based on very limited performance data for arsenic and mercury from advanced treatment information available in the technical literature, compliance with revised criteria may or may not be possible, depending upon site specific circumstances.
            - Compliance with a HHWQC for arsenic of 0.018 µg/L appears unlikely. Most treatment technology performance information available in the literature is based on drinking water treatment applications targeting a much higher Safe Drinking Water Act (SDWA) maximum contaminant level (MCL) of 10 µg/L.
            - Compliance with a HHWQC for mercury of 0.005 µg/L appears to be potentially attainable on an average basis, but perhaps not if effluent limits are structured on a maximum monthly, maximum weekly or maximum daily basis. Some secondary treatment facilities attain average effluent mercury levels of 0.009 to 0.066 µg/L. Some treatment facilities with effluent filters attain average effluent mercury levels of 0.002 to 0.010 µg/L. Additional

advanced treatment processes are expected to enhance these removal rates, but little mercury performance data is available for a definitive assessment.

- Little information is available to assess the potential for advanced technologies to comply with revised BAP criteria. A municipal wastewater treatment plant study reported both influent and effluent BAP concentrations less than the HHWQC of 0.0013 ug/L (Ecology, 2010).

- Some technologies may be effective at treating identified constituents of concern to meet revised limits while others may not. It is therefore even more challenging to identify a technology that can meet all constituent limits simultaneously.
- A HHWQC that is one order-of-magnitude less stringent could likely be met for mercury and BAP; however, it appears PCB and arsenic limits would not be met.

- Advanced treatment processes incur significant capital and operating costs.
  - Advanced treatment process to remove additional arsenic, BAP, mercury, and PCBs would combine enhancements to secondary treatment with microfiltration membranes and reverse osmosis or granular activated carbon and increase the estimated capital cost of treatment from $17 to $29 in dollars per gallon per day of capacity (based on a 5.0-million-gallon-per-day (mgd) facility).
  - The annual operation and maintenance costs for the advanced treatment process train will be substantially higher (approximately $5 million - $15 million increase for a 5.0 mgd capacity facility) than the current secondary treatment level.
- Implementation of additional treatment will result in additional collateral impacts.
  - High energy consumption.
  - Increased greenhouse gas emissions.
  - Increase in solids production from chemical addition to the primaries. Additionally, the membrane and GAC facilities will capture more solids that require handling.
  - Increased physical space requirements at treatment plant sites for advanced treatment facilities and residuals management including reverse osmosis reject brine processing.
- It appears advanced treatment technology alone cannot meet all revised water quality limits and implementation tools are necessary for discharger compliance.
  - Implementation flexibility will be necessary to reconcile the difference between the capabilities of treatment processes and the potential for HHWQC driven water quality based effluent limits to be lower than attainable with technology

Table ES-1 indicates that the unit NPV cost for baseline conventional secondary treatment ranges from $13 to $28 per gallon per day of treatment capacity. The unit cost for the advanced treatment alternatives increases the range from the low $20s to upper $70s on a per gallon per-day of treatment capacity. The resulting unit cost for improving from secondary treatment to advanced treatment ranges between $15 and $50 per gallon per day of treatment capacity. Unit costs were also evaluated for both a 0.5 and 25 mgd facility. The range of unit costs for improving a 0.5 mgd from secondary to advanced treatment is $60 to $162 per gallon per day of treatment capacity. The range of unit costs for improving a 25 mgd from secondary to advanced treatment is $10 to $35 per gallon per day of treatment capacity.

Table ES-1. Treatment Technology Costs in 2013 Dollars for a 5-mgd Facility

Alternative	Total Construction Cost, 2013 dollars ($ Million)	O&M Net Present Value, 2013 dollars ($ Million)***	Total Net Present Value, 2013 dollars ($ Million)	NPV Unit Cost, 2013 dollars ($/gpd)
Baseline (Conventional Secondary Treatment)*	59 - 127	5 - 11	65 - 138	13 - 28
Incremental Increase to Advanced Treatment - MF/RO	48 - 104	26 - 56	75 - 160	15 - 32
Advanced Treatment - MF/RO**	108 - 231	31 - 67	139 - 298	28 - 60
Incremental Increase to Advanced Treatment - MF/GAC	71 - 153	45 - 97	117 - 250	23 - 50
Advanced Treatment - MF/GAC	131 - 280	50 - 108	181 - 388	36 - 78

* Assumed existing treatment for dischargers. The additional cost to increase the SRT to upwards of 30-days is about $12 - 20 million additional dollars in total project cost for a 5 mgd design flow.

** Assumes zero liquid discharge for RO brine management, followed by evaporation ponds. Other options are available as listed in Section 4.4.2.

*** Does not include the cost for labor.

mgd=million gallons per day
MG=million gallons
MF/RO=membrane filtration/reverse osmosis
MF/GAC=membrane filtration/granulated activated carbon
O&M=operations and maintenance
Net Present Value = total financed cost assuming a 5% nominal discount rate over an assumed 25 year equipment life.

Costs presented above are based on a treatment capacity of 5.0 mgd, however, existing treatment facilities range dramatically across Washington in size and flow treated. The key differences in cost between the baseline and the advanced treatment MF/RO are as follows:

- Larger aeration basins than the baseline to account for the longer SRT (>8 days versus <8 days).
- Additional pumping stations to pass water through the membrane facilities and granulated activated carbon facilities. These are based on peak flows.
- Membrane facilities (equipment, tanks chemical feed facilities, pumping, etc.) and replacement membrane equipment.
- Granulated activated carbon facilities (equipment, contact tanks, pumping, granulated activated carbon media, etc.)
- Additional energy and chemical demand to operate the membrane and granulated activated carbon facilities
- Additional energy to feed and backwash the granulated activated carbon facilities.
- Zero liquid discharge facilities to further concentrate the brine reject.
    - Zero liquid discharge facilities are energy/chemically intensive and they require membrane replacement every few years due to the brine reject water quality.
- Membrane and granulated activated carbon media replacement represent a significant maintenance cost.

- Additional hauling and fees to regenerate granulated activated carbon off-site.

The mass of pollutant removal by implementing advanced treatment was calculated based on reducing current secondary effluent discharges to revised effluent limits for the four pollutants of concern. These results are provided in Table ES-2 as well as a median estimated unit cost basis for the mass of pollutants removed.

Table ES-2. Unit Cost by Contaminant for a 5-mgd Facility Implementing Advanced Treatment using Membrane Filtration/Reverse Osmosis

Component	PCBs	Mercury	Arsenic	BAPs
Required HHWQC based Effluent Quality (µg/L)	0.0000064	0.005	0.018	0.0013
Current Secondary Effluent Concentration (µg/L)	0.002	0.025	7.5	0.006
Total Mass Removed (lbs) over 25 year Period	0.76	7.6	2,800	1.8
Median Estimated Unit Cost (NPV per total mass removed in pounds over 25 years)	$290,000,000	$29,000,000	$77,000	$120,000,000

µg/L=micrograms per liter
lbs=pounds
NPV=net present value

Collateral adverse environmental impacts associated with implementing advanced treatment were evaluated. The key impacts from this evaluation include increased energy use, greenhouse gas production, land requirements and treatment residuals disposal. Operation of advanced treatment technologies could increase electrical energy by a factor of 2.3 to 4.1 over the baseline secondary treatment system. Direct and indirect greenhouse gas emission increases are related to the operation of advanced treatment technologies and electrical power sourcing, with increases of at least 50 to 100 percent above the baseline technology. The energy and air emission implications of advanced treatment employing granulated activated carbon construction of advanced treatment facilities will require additional land area. The availability and cost of land adjacent to existing treatment facilities has not been included in cost estimates, but could be very substantial. It is worthwhile noting residual materials from treatment may potentially be hazardous and their disposal may be challenging to permit. Costs assume zero liquid discharge from the facilities.

1.0 Introduction

Washington's Department of Ecology (Ecology) has an obligation to periodically review waterbody "designated uses" and to modify, as appropriate, water quality standards to ensure those uses are protected. Ecology initiated this regulatory process in 2009 for the human health-based water quality criteria (HHWQC) in Washington's *Surface Water Quality Standards* (Washington Administrative Code [WAC] 173-201A). HHWQC are also commonly referred to as "toxic pollutant water quality standards." Numerous factors will influence Ecology's development of HHWQC. The expectation is that the adopted HHWQC will be more stringent than current adopted criteria. National Pollutant Discharge Elimination System (NPDES) effluent limits for permitted dischargers to surface waters are based on U.S. Environmental Protection Agency (EPA) and state guidance. Effluent limits are determined primarily from reasonable potential analyses and waste load allocations (WLAs) from total maximum daily loads (TMDLs), although the permit writer may use other water quality data. Water quality-based effluent limits are set to be protective of factors, including human health, aquatic uses, and recreational uses. Therefore, HHWQC can serve as a basis for effluent limits. The presumption is that more stringent HHWQC will, in time, drive lower effluent limits. The lower effluent limits will require advanced treatment technologies and will have a consequent financial impact on NPDES permittees. Ecology anticipates that a proposed revision to the water quality standards regulation will be issued in first quarter 2014, with adoption in late 2014.

The Association of Washington Businesses (AWB) is recognized as the state's chamber of commerce, manufacturing and technology association. AWB members, along with the Association of Washington Cities and Washington State Association of Counties (collectively referred to as Study Partners), hold NPDES permits authorizing wastewater discharges. The prospect of more stringent HHWQC, and the resulting needs for advanced treatment technologies to achieve lower effluent discharge limits, has led this consortium to sponsor a study to assess technology availability and capability, capital and operations and maintenance (O&M) costs, pollutant removal effectiveness, and collateral environmental impacts of candidate technologies.

The "base case" for the study began with the identification of four nearly ubiquitous toxic pollutants present in many industrial and municipal wastewater discharges, and the specification of pollutant concentrations in well-treated secondary effluent. The pollutants are arsenic, benzo(a)pyrene (BAP), mercury and polychlorinated biphenyls (PCBs), which were selected for review based on available monitoring data and abundant presence in the environment. The purpose of this study is to review the potential water quality standards and associated treatment technologies able to meet those standards for four pollutants.

A general wastewater treatment process and wastewater characteristics were used as the common baseline for comparison with all of the potential future treatment technologies considered. An existing secondary treatment process with disinfection at a flow of 5 million gallons per day (mgd) was used to represent existing conditions. Typical effluent biochemical oxygen demand (BOD) and total suspended solids (TSS) were assumed between 10 and 30 milligrams per liter (mg/L) for such a facility and no designed nutrient or toxics removal was assumed for the baseline existing treatment process.

Following a literature review of technologies, two advanced treatment process options for toxics removal were selected for further evaluation based on the characterization of removal effectiveness from the technical literature review and Study Partners' preferences. The two tertiary treatment options are microfiltration membrane filtration (MF) followed by either reverse osmosis (RO) or granular activated carbon (GAC) as an addition to an existing secondary treatment facility.

The advanced treatment technologies are evaluated for their efficacy and cost to achieve the effluent limitations implied by the more stringent HHWQC. Various sensitivities are examined, including for less stringent adopted HHWQC, and for a size range of treatment systems. Collateral environmental impacts associated with the operation of advanced technologies are also qualitatively described.

2.0 Derivation of the Baseline Study Conditions and Rationale for Selection of Effluent Limitations

2.1 Summary of Water Quality Criteria

Surface water quality standards for toxics in the State of Washington are being updated based on revised human fish consumption rates (FCRs). The revised water quality standards could drive very low effluent limitations for industrial and municipal wastewater dischargers. Four pollutants were selected for study based on available monitoring data and abundant presence in the environment. The four toxic constituents are arsenic, BAP, mercury, and PCBs.

2.2 Background

Ecology is in the process of updating the HHWQC in the state water quality standards regulation. Toxics include metals, pesticides, and organic compounds. The human health criteria for toxics are intended to protect people who consume water, fish, and shellfish. FCRs are an important factor in the derivation of water quality criteria for toxics.

The AWB/City/County consortium (hereafter "Study Partners") has selected four pollutants for which more stringent HHWQC are expected to be promulgated. The Study Partners recognize that Ecology probably will not adopt more stringent arsenic HHWQC so the evaluation here is based on the current arsenic HHWQC imposed by the National Toxics Rule. Available monitoring information indicates these pollutants are ubiquitous in the environment and are expected to be present in many NPDES discharges. The four pollutants include the following:

- Arsenic
  - Elemental metalloid that occurs naturally and enters the environment through erosion processes. Also widely used in batteries, pesticides, wood preservatives, and semiconductors. Other current uses and legacy sources in fungicides/herbicides, copper smelting, paints/dyes, and personal care products.

- Benzo(a)pyrene (BAP)
  - Benzo(a)pyrene is a polycyclic aromatic hydrocarbon formed by a benzene ring fused to pyrene as the result of incomplete combustion. Its metabolites are highly carcinogenic. Sources include wood burning, coal tar, automobile exhaust, cigarette smoke, and char-broiled food.

- Mercury
  - Naturally occurring element with wide legacy uses in thermometers, electrical switches, fluorescent lamps, and dental amalgam. Also enters the environment through erosion processes, combustion (especially coal), and legacy industrial/commercial uses. Methylmercury is an organometallic that is a bioaccumulative toxic. In aquatic systems, an anaerobic methylation process converts inorganic mercury to methylmercury.

- Polychlorinated Biphenyls (PCBs)
  - Persistent organic compounds historically used as a dielectric and coolant in electrical equipment and banned from production in the U.S. in 1979. Available information indicates continued pollutant loadings to the environment as a byproduct from the use of some pigments, paints, caulking, motor oil, and coal combustion.

2.3 Assumptions Supporting Selected Ambient Water Quality Criteria and Effluent Limitations

Clean Water Act regulations require NPDES permittees to demonstrate their discharge will "not cause or contribute to a violation of water quality criteria." If a "reasonable potential analysis" reveals the possibility of a standards violation, the permitting authority is obliged to develop "water quality-based effluent limits" to ensure standards achievement. In addition, if ambient water quality monitoring or fish tissue assessments reveal toxic pollutant concentrations above HHWQC levels, Ecology is required to identify that impairment ("303(d) listing") and develop corrective action plans to force reduction in the toxic pollutant discharge or loading of the pollutant into the impaired water body segment. These plans, referred to as total maximum daily loads (TMDLs) or water cleanup plans, establish discharge allocations and are implemented for point discharge sources through NPDES permit effluent limits and other conditions.

The effect of more stringent HHWQC will intuitively result in more NPDES permittees "causing or contributing" to a water quality standards exceedance, and/or more waterbodies being determined to be impaired, thus requiring 303(d) listing, the development of TMDL/water cleanup plans, and more stringent effluent limitations to NPDES permittees whose treated wastewater contains the listed toxic pollutant.

The study design necessarily required certain assumptions to create a "baseline effluent scenario" against which the evaluation of advanced treatment technologies could occur. The Study Partners and HDR Engineering, Inc (HDR) developed the scenario. Details of the baseline effluent scenario are presented in Table 1. The essential assumptions and rationale for selection are presented below:

- Ecology has indicated proposed HHWQC revisions will be provided in first quarter 2014. A Study Partners objective was to gain an early view on the treatment technology and cost implications. Ecology typically allows 30 or 45 days for the submission of public comments on proposed regulations. To wait for the proposed HHWQC revisions would not allow sufficient time to complete a timely technology/cost evaluation and then to share the study results in the timeframe allowed for public involvement/public comments.
- Coincident with the issuance of the proposed regulation, Ecology has a statutory obligation to provide a Significant Legislative Rule evaluation, one element of which is a "determination whether the probable benefits of the rule are greater than its probable costs, taking into account both the qualitative and quantitative benefits and costs and the specific directives of the statute being implemented" (RCW 34.05.328(1)(d)). A statutory requirement also exists to assess the impact of the proposed regulation to small businesses. The implication is that Ecology will be conducting these economic evaluations in fourth quarter 2013 and early 2014. The Study Partners wanted to have a completed technology/cost study available to share with Ecology for their significant legislative rule/small business evaluations.
- The EPA, Indian tribes located in Washington, and various special interest groups have promoted the recently promulgated state of Oregon HHWQC (2011) as the "model" for Washington's revisions of HHWQC. The Oregon HHWQC are generally based on a increased FCR of 175 grams per day (g/day) and an excess cancer risk of 10^{-6}. While the Study Partners do not concede the wisdom or appropriateness of the Oregon criteria, or the selection of scientific/technical elements used to derive those criteria, the Study Partners nevertheless have selected the Oregon HHWQC as a viable "starting point" upon which this study could be based.

- The scenario assumes generally that Oregon's HHWQC for ambient waters will, for some parameters in fact, become effluent limitations for Washington NPDES permittees. The reasoning for this important assumption includes:
    - The state of Washington's NPDES permitting program is bound by the *Friends of Pinto Creek vs. EPA* decision in the United States Court of Appeals for the Ninth Circuit (October 4, 2007). This decision held that no NPDES permits authorizing new or expanded discharges of a pollutant into a waterbody identified as impaired; i.e., listed on CWA section 303(d), for that pollutant, may be issued until such time as "existing dischargers" into the waterbody are "subject to compliance schedules designed to bring the (waterbody) into compliance with applicable water quality standards." In essence, any new/expanded discharge of a pollutant causing impairment must achieve the HHWQC at the point of discharge into the waterbody.
    - If a waterbody segment is identified as "impaired" (i.e., not achieving a HHWQC), then Ecology will eventually need to produce a TMDL or water cleanup plan. For an existing NPDES permittee with a discharge of the pollutant for which the receiving water is impaired, the logical assumption is that any waste load allocation granted to the discharger will be at or lower than the numeric HHWQC (to facilitate recovery of the waterbody to HHWQC attainment). As a practical matter, this equates to an effluent limit established at the HHWQC.
    - Acceptance of Oregon HHWQC as the baseline for technology/cost review also means acceptance of practical implementation tools used by Oregon. The HHWQC for mercury is presented as a fish tissue methyl mercury concentration. For the purposes of NPDES permitting, however, Oregon has developed an implementation management directive which states that any confirmed detection of mercury is considered to represent a "reasonable potential" to cause or contribute to a water quality standards violation of the methyl mercury criteria. The minimum quantification level for total mercury is presented as 0.005 micrograms per liter (µg/L) (5.0 nanograms per liter (ng/L)).
    - The assumed effluent limit for arsenic is taken from EPA's *National Recommended Water Quality Criteria* (2012) (inorganic, water and organisms, 10^{-6} excess cancer risk). Oregon's 2011 criterion is actually based on a less protective excess cancer risk (10^{-4}). This, however, is the result of a state-specific risk management choice and it is unclear if Washington's Department of Ecology would mimic the Oregon approach.
    - The assumption is that no mixing zone is granted such that HHWQC will effectively serve as NPDES permit effluent limits. Prior discussion on the impact of the Pinto Creek decision, 303(d) impairment and TMDL Waste Load Allocations processes, all lend support to this "no mixing zone" condition for the parameters evaluated in this study.
- Consistent with Ecology practice in the evaluation of proposed regulations, the HHWQC are assumed to be in effect for a 20-year period. It is assumed that analytical measurement technology and capability will continue to improve over this time frame and this will result in the detection and lower quantification of additional HHWQC in ambient water and NPDES dischargers. This knowledge will trigger the Pinto Creek/303(d)/TMDL issues identified above and tend to pressure NPDES permittees to evaluate and install advanced treatment technologies. The costs and efficacy of treatment for these additional HHWQC is unknown at this time.

Other elements of the Study Partners work scope, as presented to HDR, must be noted:

- The selection of four toxic pollutants and development of a baseline effluent scenario is not meant to imply that each NPDES permittee wastewater discharge will include those pollutants at the assumed concentrations. Rather, the scenario was intended to represent a composite of many NPDES permittees and to facilitate evaluation of advanced treatment technologies relying on mechanical, biological, physical, chemical processes.
- The scalability of advanced treatment technologies to wastewater treatment systems with different flow capacities, and the resulting unit costs for capital and O&M, is evaluated.
- Similarly, a sensitivity analysis on the unit costs for capital and O&M was evaluated on the assumption the adopted HHWQC (and effectively, NPDES effluent limits) are one order-of-magnitude less stringent than the Table 1 values.

Table 1: Summary of Effluent Discharge Toxics Limits

Constituent	Human Health Criteria based Limits to be met with no Mixing Zone (µg/L)	Basis for Criteria	Typical Concentration in Municipal Secondary Effluent (µg/L)	Typical Concentration in Industrial Secondary Effluent (µg/L)	Existing Washington HHC (water + org.), NTR (µg/L)
PCBs	0.0000064	Oregon Table 40 Criterion (water + organisms) at FCR of 175 grams/day	0.0005 to 0.0025[b,c,d,e,f]	0.002 to 0.005[i]	0.0017
Mercury	0.005	DEQ IMD[a]	0.003 to 0.050[h]	0.010 to 0.050[h]	0.140
Arsenic	0.018	EPA National Toxics Rule (water + organisms)[k]	0.500 to 5.0[j]	10 to 40[j]	0.018
Benzo(a)Pyrene	0.0013	Oregon Table 40 Criterion (water + organisms) at FCR of 175 grams/day	0.00028 to 0.006[b,g]	0.006 to1.9	0.0028

[a] Oregon Department of Environmental Quality (ODEQ). Internal Management Directive: Implementation of Methylmercury Criterion in NPDES Permits. January 8, 2013.
[b] Control of Toxic Chemicals in Puget Sound, Summary Technical Report for Phase 3: Loadings from POTW Discharge of Treated Wastewater, Washington Department of Ecology, Publication Number 10-10-057, December 2010.
[c] Spokane River PCB Source Assessment 2003-2007, Washington Department of Ecology, Publication No. 11-03-013, April 2011.
[d] Lower Okanogan River Basin DDT and PCBs Total Maximum Daily Load, Submittal Report, Washington Department of Ecology, Publication Number 04-10-043, October 2004.
[e] Palouse River Watershed PCB and Dieldrin Monitoring, 2007-2008, Wastewater Treatment Plants and Abandoned Landfills, Washington Department of Ecology, Publication No. 09-03-004, January 2009
[f] A Total Maximum Daily Load Evaluation for Chlorinated Pesticides and PCBs in the Walla Walla River, Washington Department of Ecology, Publication No. 04-03-032, October 2004.
[g] Removal of Polycyclic Aromatic Hydrocarbons and Heterocyclic Nitrogenous Compounds by A POTW Receiving Industrial Discharges, Melcer, H., Steel, P. and Bedford, W.K., Water Environment Federation, 66th Annual Conference and Exposition, October 1993.
[h] Data provided by Lincoln Loehr's summary of WDOE Puget Sound Loading data in emails from July 19, 2013.
[i] NCASI memo from Larry Lefleur, NCASI, to Llewellyn Matthews, NWPPA, revised June 17, 2011, summarizing available PCB monitoring data results from various sources.
[j] Professional judgment, discussed in August 6, 2013 team call.
[k] The applicable Washington Human Health Criteria cross-reference the EPA National Toxics Rule, 40 CFR 131.36. The EPA arsenic HHC is 0.018 ug/L for water and organisms.

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3.0 Wastewater Characterization Description

This section describes the wastewater treatment discharge considered in this technology evaluation. Treated wastewater characteristics are described, including average and peak flow, effluent concentrations, and toxic compounds of concern.

3.1 Summary of Wastewater Characterization

A general wastewater treatment process and wastewater characteristics were developed as the common baseline to represent the existing conditions as a starting point for comparison with potential future advanced treatment technologies and improvements. A secondary treatment process with disinfection at a flow of 5 mgd as the current, baseline treatment system for existing dischargers was also developed. Typical effluent biochemical oxygen demand (BOD) and total suspended solids (TSS) were assumed between 10 to 30 mg/L from such a facility and no nutrient or toxics removal was assumed to be accomplished in the existing baseline treatment process.

3.2 Existing Wastewater Treatment Facility

The first step in the process is to characterize the existing wastewater treatment plant to be evaluated in this study. The goal is to identify the necessary technology that would need to be added to an existing treatment facility to comply with revised toxic pollutant effluent limits. Rather than evaluating the technologies and costs to upgrade multiple actual operating facilities, the Study Partners specified that a generalized municipal/industrial wastewater treatment facility would be characterized and used as the basis for developing toxic removal approaches. General characteristics of the facility's discharge are described in Table 2.

Table 2. General Wastewater Treatment Facility Characteristics

Average Annual Wastewater Flow, mgd	Maximum Month Wastewater Flow, mgd	Peak Hourly Wastewater Flow, mgd	Effluent BOD, mg/L	Effluent TSS, mg/L
5.0	6.25	15.0	10 to 30	10 to 30

mgd=million gallons per day
mg/L=milligrams per liter
BOD=biochemical oxygen demand
TSS=total suspended solids

In the development of the advanced treatment technologies presented below, the capacity of major treatment elements are generally sized to accommodate the maximum month average wastewater flow. Hydraulic elements, such as pumps and pipelines, were selected to accommodate the peak hourly wastewater flow.

The general treatment facility incorporates a baseline treatment processes including influent screening, grit removal, primary sedimentation, suspended growth biological treatment (activated sludge), secondary clarification, and disinfection using chlorine. Solids removed during primary treatment and secondary clarification are assumed to be thickened, stabilized, dewatered, and land applied to agricultural land. The biological treatment process is assumed to be activated sludge with a relatively short (less than 10-day) solids retention time. The baseline secondary treatment facility is assumed not to have processes dedicated to removing nutrients or toxics. However, some coincident removal of toxics will occur during conventional treatment.

3.3 Toxic Constituents

As described in Section 2.3, the expectation of more stringent HHWQC will eventually trigger regulatory demands for NPDES permittees to install advanced treatment technologies. The Study Group and HDR selected four specific toxic pollutants reflecting a range of toxic constituents as the basis for this study to limit the constituents and technologies to be evaluated to a manageable level.

The four toxic pollutants selected were PCBs, mercury, arsenic, and BAP, a polycyclic aromatic hydrocarbon (PAH). Mercury and arsenic are metals, and PCBs and PAHs are organic compounds. Technologies for removing metals and organic compounds are in some cases different. Key information on each of the compounds, including a description of the constituent, the significance of each constituent, proposed HHWQC, basis for the proposed criteria, typical concentration in both municipal and industrial secondary effluent, and current Washington state water quality criteria, are shown in Table 1. It is assumed that compliance with the proposed criteria in the table would need to be achieved at the “end of pipe” and Ecology would not permit a mixing zone for toxic constituents. This represents a “worst–case,” but a plausible assumption about discharge conditions.

4.0 Treatment Approaches and Costs

4.1 Summary of Treatment Approach and Costs

Two advanced treatment process options for toxics removal for further evaluation based on the characterization of removal effectiveness from the technical literature review and Study Group preferences. The two tertiary treatment options are microfiltration MF followed by either RO or GAC as an addition to an existing secondary treatment facility. Based on the literature review, it is not anticipated that any of the treatment options will be effective in reducing all of the selected pollutants to below the anticipated water quality criteria. A summary of the capital and operations and maintenance costs for tertiary treatment is provided, as well as a comparison of the adverse environmental impacts for each alternative.

4.2 Constituent Removal – Literature Review

The evaluation of treatment technologies relevant to the constituents of concern was initiated with a literature review. The literature review included a desktop search using typical web-based search engines, and search engines dedicated to technical and research journal databases. At the same time, HDR's experience with the performance of existing treatment technologies specifically related to the four constituents of concern, was used in evaluating candidate technologies. A summary of the constituents of concern and relevant treatment technologies is provided in the following literature review section.

4.2.1 Polychlorinated Biphenyls

PCBs are persistent organic pollutants that can be difficult to remove in treatment. PCB treatment in wastewater can be achieved using oxidation with peroxide, filtration, biological treatment or a combination of these technologies. There is limited information available about achieving ultra-low effluent PCB concentrations near the 0.0000064 µg/L range under consideration in the proposed rulemaking process. This review provides a summary of treatment technology options and anticipated effluent PCB concentrations.

Research on the effectiveness of ultraviolet (UV) light and peroxide on removing PCBs was tested in bench scale batch reactions (Yu, Macawile, Abella, & Gallardo 2011). The combination of UV and peroxide treatment achieved PCB removal greater than 89 percent, and in several cases exceeding 98 percent removal. The influent PCB concentration for the batch tests ranged from 50 to 100 micrograms per liter (µg/L). The final PCB concentration (for the one congener tested) was <10 µg/L (10,000 ng/L) for all tests and <5 µg/L (5,000 ng/L) for some tests. The lowest PCB concentrations in the effluent occurred at higher UV and peroxide doses.

Pilot testing was performed to determine the effectiveness of conventional activated sludge and a membrane bioreactor to remove PCBs (Bolzonella, Fatone, Pavan, & Cecchi 2010). EPA Method 1668 was used for the PCB analysis (detection limit of 0.01 ng/L per congener). Influent to the pilot system was a combination of municipal and industrial effluent. The detailed analysis was for several individual congeners. Limited testing using the Aroclor method (total PCBs) was used to compare the individual congeners and the total concentration of PCBs. Both conventional activated sludge and membrane bioreactor (MBR) systems removed PCBs. The effluent MBR concentrations ranged from <0.01 ng/L to 0.04 ng/L compared to <0.01 ng/L to 0.88 ng/L for conventional activated sludge. The pilot testing showed that increased solids retention time (SRT) and higher mixed liquor suspended solids concentrations in the MBR system led to increased removal in the liquid stream.

Bench scale studies were completed to test the effectiveness of GAC and biological activated carbon (BAC) for removing PCBs (Ghosh, Weber, Jensen, & Smith 1999). The effluent from the

GAC system was 800 ng/L. The biological film in the BAC system was presumed to support higher PCB removal with effluent concentrations of 200 ng/L. High suspended sediment in the GAC influent can affect performance. It is recommended that filtration be installed upstream of a GAC system to reduce solids and improve effectiveness.

Based on limited available data, it appears that existing municipal secondary treatment facilities in Washington state are able to reduce effluent PCBs to the range approximately 0.10 to 1.5 ng/L. It appears that the best performing existing municipal treatment facility in Washington state with a microfiltration membrane is able to reduce effluent PCBs to the range approximately 0.00019 to 0.00063 µg/L. This is based on a very limited data set and laboratory blanks covered a range that overlapped with the effluent results (blanks 0.000058 to 0.00061 µg/L).

Addition of advanced treatment processes would be expected to enhance PCB removal rates, but the technical literature does not appear to provide definitive information for guidance. A range of expected enhanced removal rates might be assumed to vary widely from level of the reference microfiltration facility of 0.19 to 0.63 ng/L.

Summary of PCB Technologies

The literature review revealed there are viable technologies available to reduce PCBs **but no research was identified with treatment technologies capable of meeting the anticipated human health criteria based limits for PCB removal**. Based on this review, a tertiary process was selected to biologically reduce PCBs and separate the solids using tertiary filtration. Alternately, GAC was investigated as an option to reduce PCBs, although it is not proven that it will meet revised effluent limits.

4.2.2 Mercury

Mercury removal from wastewater can be achieved using precipitation, adsorption, filtration, or a combination of these technologies. There is limited information available about achieving ultra-low effluent mercury concentrations near the 5 ng/L range under consideration in the proposed rulemaking process. This review provides a summary of treatment technology options and anticipated effluent mercury concentrations.

Precipitation (and co-precipitation) involves chemical addition to form a particulate and solids separation, using sedimentation or filtration. Precipitation includes the addition of a chemical precipitant and pH adjustment to optimize the precipitation reaction. Chemicals can include metal salts (ferric chloride, ferric sulfate, ferric hydroxide, or alum), pH adjustment, lime softening, or sulfide. A common precipitant for mercury removal is sulfide, with an optimal pH between 7 and 9. The dissolved mercury is precipitated with the sulfide to form an insoluble mercury sulfide that can be removed through clarification or filtration. One disadvantage of precipitation is the generation of a mercury-laden sludge that will require dewatering and disposal. The mercury sludge may be considered a hazardous waste and require additional treatment and disposal at a hazardous waste site. The presence of other compounds, such as other metals, may reduce the effectiveness of mercury precipitation/co-precipitation. For low-level mercury treatment requirements, several treatment steps will likely be required in pursuit of very low effluent targets.

EPA compiled a summary of facilities that are using precipitation/co-precipitation for mercury treatment (EPA 2007). Three of the full-scale facilities were pumping and treating groundwater and the remaining eight facilities were full-scale wastewater treatment plants. One of the pump and treat systems used precipitation, carbon adsorption, and pH adjustment to treat groundwater to effluent concentrations of 300 ng/L.

Adsorption treatment can be used to remove inorganic mercury from water. While adsorption can be used as a primary treatment step, it is frequently used for polishing after a preliminary treatment step (EPA 2007). One disadvantage of adsorption treatment is that when the adsorbent is saturated, it either needs to be regenerated or disposed of and replaced with new adsorbent. A common adsorbent is GAC. There are several patented and proprietary adsorbents on the market for mercury removal. Adsorption effectiveness can be affected by water quality characteristics, including high solids and bacterial growth, which can cause media blinding. A constant and low flow rate to the adsorption beds increases effectiveness (EPA 2007). The optimal pH for mercury adsorption on GAC is pH 4 to 5; therefore, pH adjustment may be required.

EPA compiled a summary of facilities that are using adsorption for mercury treatment (EPA 2007). Some of the facilities use precipitation and adsorption as described above. The six summarized facilities included two groundwater treatment and four wastewater treatment facilities. The reported effluent mercury concentrations were all less than 2,000 ng/L (EPA 2007).

Membrane filtration can be used in combination with a preceding treatment step. The upstream treatment is required to precipitate soluble mercury to a particulate form that can be removed through filtration. According to the EPA summary report, ultrafiltration is used to remove high-molecular weigh contaminants and solids (EPA 2007). The treatment effectiveness can depend on the source water quality since many constituents can cause membrane fouling, decreasing the effectiveness of the filters. One case study summarized in the EPA report showed that treatment of waste from a hazardous waste combustor treated with precipitation, sedimentation, and filtration achieved effluent mercury concentrations less than the detection limit of 200 ng/L.

Bench-scale research performed at the Oak Ridge Y-12 Plant in Tennessee evaluated the effectiveness of various adsorbents for removing mercury to below the NPDES limit of 12 ng/L and the potential revised limit of 51 ng/L (Hollerman et al. 1999). Several proprietary adsorbents were tested, including carbon, polyacrylate, polystyrene, and polymer adsorption materials. The adsorbents with thiol-based active sites were the most effective. Some of the adsorbents were able to achieve effluent concentrations less than 51 ng/L but none of the adsorbents achieved effluent concentrations less than 12 ng/L.

Bench-scale and pilot-scale testing performed on refinery wastewater was completed to determine treatment technology effectiveness for meeting very low mercury levels (Urgun-Demirtas, Benda, Gillenwater, Negri, Xiong & Snyder 2012) (Urgun-Demirtas, Negri, Gillenwater, Agwu Nnanna & Yu 2013). The Great Lakes Initiative water quality criterion for mercury is less than 1.3 ng/L for municipal and industrial wastewater plants in the Great Lakes region. This research included an initial bench scale test including membrane filtration, ultrafiltration, nanofiltration, and reverse osmosis to meet the mercury water quality criterion. The nanofiltration and reverse osmosis required increased pressures for filtration and resulted in increased mercury concentrations in the permeate. Based on this information and the cost difference between the filtration technologies, a pilot-scale test was performed. The 0.04 um PVDF GE ZeeWeed 500 series membranes were tested. The 1.3 ng/L water quality criterion was met under all pilot study operating conditions. The mercury in the refinery effluent was predominantly in particulate form which was well-suited for removal using membrane filtration.

Based on available data, it appears that existing municipal treatment facilities are capable of reducing effluent mercury to near the range of the proposed HHWQC on an average basis. Average effluent mercury in the range of 1.2 to 6.6 ng/L for existing facilities with secondary treatment and enhanced treatment with cloth filters and membranes. The Spokane County plant data range is an average of 1.2 ng/L to a maximum day of 3 ng/L. Addition of

advanced treatment processes such as GAC or RO would be expected to enhance removal rates. Data from the West Basin treatment facility in California suggests that at a detection limit of 7.99 ng/L mercury is not detected in the effluent from this advanced process train. A range of expected enhanced removal rates from the advanced treatment process trains might be expected to ranged from meeting the proposed standard at 5 ng/L to lower concentrations represented by the Spokane County performance level (membrane filtration) in the range of 1 to 3 ng/L, to perhaps even lower levels with additional treatment. For municipal plants in Washington, this would suggest that effluent mercury values from the two advanced treatment process alternatives might range from 1 to 5 ng/L (0.001 to 0.005 µg/L) and perhaps substantially better, depending upon RO and GAC removals. It is important to note that industrial plants may have higher existing mercury levels and thus the effluent quality that is achievable at an industrial facility would be of lower quality.

Summary of Mercury Technologies

The literature search revealed limited research on mercury removal technologies at the revised effluent limit of 0.005 µg/L. Tertiary filtration with membrane filters or reverse osmosis showed the best ability to achieve effluent criteria less than 0.005 µg/L.

4.2.3 Arsenic

A variety of treatment technologies can be applied to capture arsenic (Table 3). Most of the information in the technical literature and from the treatment technology vendors is focused on potable water treatment for compliance with a Safe Drinking Water Act (SDWA) maximum contaminant level (MCL) of 10 µg/L. The most commonly used arsenic removal method for a wastewater application (tertiary treatment) is coagulation/ flocculation plus filtration. This method by itself could remove more than 90 to 95 percent of arsenic. Additional post-treatment through adsorption, ion exchange, or reverse osmosis is required for ultra-low arsenic limits in the 0.018 µg/L range under consideration in the proposed rulemaking process. In each case it is recommended to perform pilot-testing of each selected technology.

Table 3: Summary of Arsenic Removal Technologies[1]

Technology	Advantages	Disadvantages
Coagulation/filtration	• Simple, proven technology • Widely accepted • Moderate operator training	• pH sensitive • Potential disposal issues of backwash waste • As^{+3} and As^{+5} must be fully oxidized
Lime softening	• High level arsenic treatment • Simple operation change for existing lime softening facilities	• pH sensitive (requires post treatment adjustment) • Requires filtration • Significant sludge operation
Adsorptive media	• High As^{+5} selectivity • Effectively treats water with high total dissolved solids (TDS)	• Highly pH sensitive • Hazardous chemical use in media regeneration • High concentration SeO_4^{-2}, F^-, Cl^-, and SO_4^{-2} may limit arsenic removal

Table 3: Summary of Arsenic Removal Technologies[1]

Technology	Advantages	Disadvantages
Ion exchange	• Low contact times • Removal of multiple anions, including arsenic, chromium, and uranium	• Requires removal of iron, manganese, sulfides, etc. to prevent fouling • Brine waste disposal
Membrane filtration	• High arsenic removal efficiency • Removal of multiple contaminants	• Reject water disposal • Poor production efficiency • Requires pretreatment

[1]Adapted from WesTech

The removal of arsenic in activated sludge is minimal (less than 20 percent) (Andrianisa et al. 2006), but biological treatment can control arsenic speciation. During aerobic biological process As (III) is oxidized to As (V). Coagulation/flocculation/filtration removal, as well as adsorption removal methods, are more effective in removal of As(V) vs. As (III). A combination of activated sludge and post-activated sludge precipitation with ferric chloride (addition to MLSS and effluent) results in a removal efficiency of greater than 95 percent. This combination could decrease As levels from 200 µg/L to less than 5 µg/L (5,000 ng/L) (Andrianisa et al. 2008) compared to the 0.018 µg/L range under consideration in the proposed rulemaking process.

Data from the West Basin facility (using MF/RO/AOP) suggests effluent performance in the range of 0.1 to 0.2 µg/L, but it could also be lower since a detection limit used there of 0.15 µg/l is an order of magnitude higher than the proposed HHWQC. A range of expected enhanced removal rates might be assumed to equivalent to that achieved at West Basin in 0.1 to 0.2 µg/L range.

Review of Specific Technologies for Arsenic Removal

Coagulation plus Settling or Filtration

Coagulation may remove more than 95 percent of arsenic through the creation of particulate metal hydroxides. Ferric sulfite is typically more efficient and applicable to most wastewater sources compared to alum. The applicability and extent of removal should be pilot-tested, since removal efficiency is highly dependent on the water constituents and water characteristics (i.e., pH, temperature, solids).

Filtration can be added after or instead of settling to increase arsenic removal. Example treatment trains with filtration are shown in Figures 1 and 2, respectively.

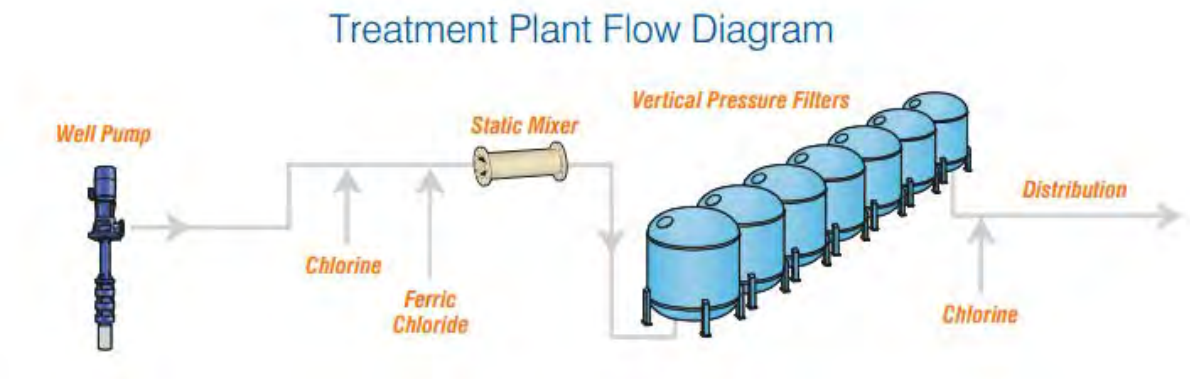

Figure 1. Water Treatment Configuration for Arsenic Removal (WesTech)

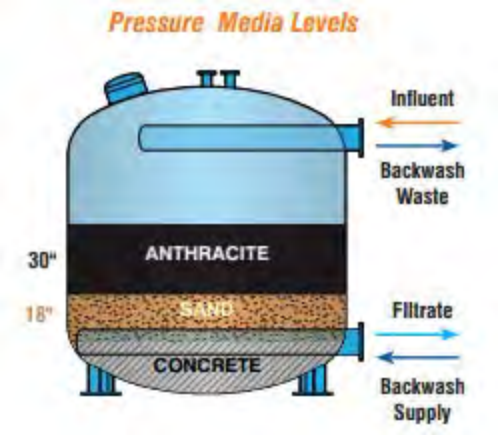

Figure 2. WesTech Pressure Filters for Arsenic Removal

One system for treatment of potable water with high levels of arsenic in Colorado (110 parts per million [ppm]) consists of enhanced coagulation followed by granular media pressure filters that include anthracite/silica sand/garnet media (WesTech). The arsenic levels were reduced to less than the drinking water MCL, which is 10 µg/L (10,000 ng/L). The plant achieves treatment by reducing the pH of the raw water to 6.8 using sulfuric acid, and then adding approximately 12 to 14 mg/L ferric sulfate. The water is filtered through 16 deep bed vertical pressure filters, the pH is elevated with hydrated lime and is subsequently chlorinated and fed into the distribution system.
(http://www.westechinc.com/public/uploads/global/2011/3/Fallon%20NV%20Installation%20ReportPressureFilter.pdf).

Softening (with lime)

Removes up to 90 percent arsenic through co-precipitation, but requires pH to be higher than 10.2.

Adsorption processes

Activated alumina is considered an adsorptive media, although the chemical reaction is an exchange of arsenic ions with the surface hydroxides on the alumina. When all the surface hydroxides on the alumina have been exchanged, the media must be regenerated. Regeneration consists of backwashing, followed by sodium hydroxide, flushing with water and neutralization with a strong acid. Effective arsenic removal requires sufficient empty bed contact time. Removal efficiency can also be impacted by the water pH, with neutral or slightly acidic conditions being considered optimum. If As (III) is present, it is generally advisable to increase empty bed contact time, as As (III) is adsorbed more slowly than As (V). Alumina dissolves slowly over time due to contact with the chemicals used for regeneration. As a result, the media bed is likely to become compacted if it is not backwashed periodically.

Granular ferric hydroxide works by adsorption, but when the media is spent it cannot be regenerated and must be replaced. The life of the media depends upon pH of the raw water, the concentrations of arsenic and heavy metals, and the volume of water treated daily. Periodic backwashing is required to prevent the media bed from becoming compacted and pH may need to be adjusted if it is high, in order to extend media life. For maximum arsenic removal, filters operate in series. For less stringent removal, filters can operate in parallel.

One type of adsorption media has been developed for application to non-drinking water processes for arsenic, phosphate and for heavy metals removal by sorption (Severent Trent Bayoxide® E IN-20). This granular ferric oxide media has been used for arsenic removal from

mining and industrial wastewaters, selenium removal from refinery wastes and for phosphate polishing of municipal wastewaters. Valley Vista drinking water treatment with Bayoxide® E IN-20 media achieves removal from 31-39 µg/L (31,000-39,000 ng/L) to below 10 µg/L MCL (http://www.severntrentservices.com/News/Successful_Drinking_Water_Treatment_in_an_Arsenic__Hot_Spot__nwMFT_452.aspx).

Another adsorptive filter media is greensand. Greensand is available in two forms: as glauconite with manganese dioxide bound ionically to the granules and as silica sand with manganese dioxide fused to the granules. Both forms operate in pressure filters and both are effective. Greensand with the silica sand core operates at higher water temperatures and higher differential pressures than does greensand with the glauconite core. Arsenic removal requires a minimum concentration of iron. If a sufficient concentration of iron is not present in the raw water, ferric chloride is added.

WesTech filters with greensand and permanganate addition for drinking water systems can reduce As from 15-25 µg/L to non-detect. Sodium hypochlorite and/or potassium permanganate are added to the raw water prior to the filters. Chemical addition may be done continuously or intermittently, depending on raw water characteristics. These chemicals oxidize the iron in the raw water and also maintain the active properties of the greensand itself. Arsenic removal is via co-precipitation with the iron.

Ion Exchange

Siemens offers a potable ion exchange (PIX) arsenic water filtration system. PIX uses ion exchange resin canisters for the removal of organic and inorganic contaminants, in surface and groundwater sources to meet drinking water standards.

Filtronics also uses ion exchange to treat arsenic. The technology allows removal for below the SWDA MCL for potable water of 10 µg/L (10,000 ng/L).

Reverse osmosis

Arsenic is effectively removed by RO when it is in oxidative state As(V) to approximately 1,000 ng/L or less (Ning 2002).

Summary of Arsenic Technologies

The current state of the technology for arsenic removal is at the point where all the processes target the SWDA MCL for arsenic in potable water. Current EPA maximum concentration level for drinking water is 10 ug/l; much higher than 0.0018 µg/L target for arsenic in this study. The majority of the methods discussed above are able to remove arsenic to either EPA maximum contaminant level or to the level of detection. The lowest detection limit of one of the EPA approved methods of arsenic measurements is 20 ng/l (0.020 µg/l) (Grosser, 2010), which is comparable to the 0.018 µg/L limit targeted in this study.

4.2.1 Polycyclic Aromatic Hydrocarbons

BAP During Biological Treatment

During wastewater treatment process, BAP tends to partition into sludge organic matter (Melcer et al. 1993). Primary and secondary processing could remove up to 60 percent of incoming PAHs and BAP in particular, mostly due to adsorption to sludge (Kindaichi et al., NA, Wayne et al. 2009). Biodegradation of BAP is expected to be very low since there are more than five benzene rings which are resistant to biological degradation. Biosurfactant addition to biological process could partially improve biodegradation, but only up to removal rates of 50 percent (Sponza et al. 2010). Existing data from municipal treatment facilities in Washington state have

influent and effluent concentrations of BAP of approximately 0.30 ng/L indicating that current secondary treatment has limited effectiveness at BAP removal.

Methods to Enhance Biological Treatment of BAP

Ozonation prior to biological treatment could potentially improve biodegradability of BAP (Zeng et al. 2000). In the case of soil remediation, ozonation before biotreatment improved biodegradation by 70 percent (Russo et al. 2012). The overall removal of BAP increased from 23 to 91 percent after exposure of water to 0.5 mg/L ozone for 30 minutes during the simultaneous treatment process and further to 100 percent following exposure to 2.5 mg/L ozone for 60 minutes during the sequential treatment mode (Yerushalmi et al. 2006). In general, to improve biodegradability of BAP, long exposure to ozone might be required (Haapea et al. 2006).

Sonication pre-treatment or electronic beam irradiation before biological treatment might also make PAHs more bioavailable for biological degradation..

Recent studies reported that a MBR is capable of removing PAHs from wastewater (Rodrigue and Reilly 2009; Gonzaleza et al. 2012). None of the studies listed the specific PAHs constituents removed.

Removal of BAP from Drinking Water

Activated Carbon

Since BAP has an affinity to particulate matter, it is removed from the drinking water sources by means of adsorption, such as granular activated carbon (EPA). Similarly, Oleszczuk et al. (2012) showed that addition of 5 percent activated carbon could remove 90 percent of PAHs from the wastewater.

Reverse Osmosis

Light (1981) (referenced by Williams, 2003) studied dilute solutions of PAHs, aromatic amines, and nitrosamines and found rejections of these compounds in reverse osmosis to be over 99 percent for polyamide membranes. Bhattacharyya et al. (1987) (referenced by Williams, 2003) investigated rejection and flux characteristics of FT30 membranes for separating various pollutants (PAHs, chlorophenols, nitrophenols) and found membrane rejections were high (>98 percent) for the organics under ionized conditions.

Summary of BAP Technologies

Current technologies show that BAP removal may be 90 percent or greater. The lowest detection limit for BAP measurements is 0.006 µg/L, which is also the assumed secondary effluent BAP concentration assumed for this study. If this assumption is accurate, it appears technologies may exist to remove BAP to a level below the proposed criteria applied as an effluent limit of 0.0013 µg/L; however, detection limits exceed this value and it is impossible to know this for certain. A municipal wastewater treatment plant study reported both influent and effluent BAP concentrations less than the HHWQC of 0.0013 ug/L (Ecology, 2010).

4.3 Unit Processes Evaluated

Based on the results of the literature review, a wide range of technologies were evaluated for toxic constituent removal. A listing of the technologies is as follows:

- Chemically enhanced primary treatment (CEPT): this physical and chemical technology is based on the addition of a metal salt to precipitate particles prior to primary treatment, followed by sedimentation of particles in the primary clarifiers. This technology has been

shown to effectively remove arsenic but there is little data supporting the claims. As a result, the chemical facilities are listed as optional.

- Activated sludge treatment (with a short SRT of approximately 8 days or less): this biological technology is commonly referred to as secondary treatment. It relies on converting dissolved organics into solids using biomass. Having a short SRT is effective at removing degradable organics referred to as BOD compounds for meeting existing discharge limits. Dissolved constituents with a high affinity to adsorb to biomass (e.g., metals, high molecular weight organics, and others) will be better removed compared to smaller molecular weight organics and recalcitrant compounds which will have minimal removal at a short SRT.
- Enhanced activated sludge treatment (with a long SRT of approximately 8 days or more): this technology builds on secondary treatment by providing a longer SRT, which enhances sorption and biodegradation. The improved performance is based on having more biomass coupled with a more diverse biomass community, especially nitrifiers, which have been shown to assist in removal of some of the more recalcitrant constituents not removed with a shorter SRT (e.g., lower molecular weight PAHs). There is little or no data available on the effectiveness of this treatment for removing BAP.

  Additional benefits associated with having a longer SRT are as follows:

  - Lower BOD/TSS discharge load to receiving water
  - Improved water quality and benefit to downstream users
  - Lower effluent nutrient concentrations which reduce algal growth potential in receiving waters
  - Reduced receiving water dissolved oxygen demand due to ammonia removal
  - Reduced ammonia discharge, which is toxic to aquatic species
  - Improved water quality for habitat, especially as it relates to biodiversity and eutrophication
  - Secondary clarifier effluent more conditioned for filtration and disinfection
  - Greater process stability from the anaerobic/anoxic zones serving as biological selectors
- Coagulation/Flocculation and Filtration: this two-stage chemical and physical process relies on the addition of a metal salt to precipitate particles in the first stage, followed by the physical removal of particles in filtration. This technology lends itself to constituents prone to precipitation (e.g., arsenic).
- Lime Softening: this chemical process relies on increasing the pH as a means to either volatilize dissolved constituents or inactivate pathogens. Given that none of the constituents being studied are expected to volatilize, this technology was not carried forward.
- Adsorptive Media: this physical and chemical process adsorbs constituents to a combination of media and/or biomass/chemicals on the media. There are several types of media, with the most proven and common being GAC. GAC can also serve as a coarse roughing filter.
- Ion Exchange: this chemical technology exchanges targeted constituents with a resin. This technology is common with water softeners where the hard divalent cations are

exchanged for monovalent cations to soften the water. Recently, resins that target arsenic and mercury removal include activated alumina and granular ferric hydroxides have been developed. The resin needs to be cleaned and regenerated, which produces a waste slurry that requires subsequent treatment and disposal. As a result, ion exchange was not considered for further.

- Membrane Filtration: This physical treatment relies on the removal of particles larger than the membranes pore size. There are several different membrane pore sizes as categorized below.
  - Microfiltration (MF): nominal pore size range of typically between 0.1 to 1 micron. This pore size targets particles, both inert and biological, and bacteria. If placed in series with coagulation/flocculation upstream, dissolved constituents precipitated out of solution and bacteria can be removed by the MF membrane.
  - Ultrafiltration (UF): nominal pore size range of typically between 0.01 to 0.1 micron. This pore size targets those solids removed with MF (particles and bacteria) plus viruses and some colloidal material. If placed in series with coagulation/flocculation upstream, dissolved constituents precipitated out of solution can be removed by the UF membrane.
  - Nanofiltration (NF): nominal pore size range of typically between 0.001 to 0.010 micron. This pore size targets those removed with UF (particles, bacteria, viruses) plus colloidal material. If placed in series with coagulation/flocculation upstream, dissolved constituents precipitated out of solution can be removed by the NF membrane.
- MBR (with a long SRT): this technology builds on secondary treatment whereby the membrane (microfiltration) replaces the secondary clarifier for solids separation. As a result, the footprint is smaller, the mixed liquor suspended solids concentration can be increased to about 5,000 – 10,000 mg/L, and the physical space required for the facility reduced when compared to conventional activated sludge. As with the activated sludge option operated at a longer SRT, the sorption and biodegradation of organic compounds are enhanced in the MBR process. The improved performance is based on having more biomass coupled with a more diverse biomass community, especially nitrifiers which have been shown to assist in removal of persistent dissolved compounds (e.g., some PAHs). There is little or no data available on effectiveness at removing BAP. Although a proven technology, MBRs were not carried further in this technology review since they are less likely to be selected as a retrofit for an existing activated sludge (with a short SRT) secondary treatment facility. The MBR was considered to represent a treatment process approach more likely to be selected for a new, greenfield treatment facility. Retrofits to existing secondary treatment facilities can accomplish similar process enhancement by extending the SRT in the activated sludge process followed by the addition of tertiary membrane filtration units.
- RO: This physical treatment method relies on the use of sufficient pressure to osmotically displace water across the membrane surface while simultaneously rejecting most salts. RO is very effective at removing material smaller than the size ranges for the membrane filtration list above, as well as salts and other organic compounds. As a result, it is expected to be more effective than filtration and MBR methods described above at removing dissolved constituents. Although effective, RO produces a brine reject water that must be managed and disposed.

- Advanced Oxidation Processes (AOPs): this broad term considers all chemical and physical technologies that create strong hydroxyl-radicals. Examples of AOPs include Fenton's oxidation, ozonation, ultraviolet/hydrogen peroxide (UV-H2O2), and others. The radicals produced are rapid and highly reactive at breaking down recalcitrant compounds. Although effective at removing many complex compounds such as those evaluated in this study, AOPs does not typically have as many installations as membranes and activated carbon technologies. As a result, AOPs were not carried forward.

Based on the technical literature review discussed above, a summary of estimated contaminant removal rated by unit treatment process is presented in Table 4.

Table 4. Contaminants Removal Breakdown by Unit Process

Unit Process	Arsenic	BAP	Mercury	Polychlorinated Biphenyls
Activated Sludge Short SRT	No removal	Partial Removal by partitioning		80% removal; effluent <0.88 ng/L
Activated Sludge Long SRT	No removal	Partial removal by partitioning and/or partially biodegradation; MBR could potentially remove most of BAP		>90% removal with a membrane bioreactor, <0.04 ng/L (includes membrane filtration)
Membrane Filtration (MF)	More than 90 % removal (rejection of bound arsenic)	No removal	<1.3 ng/L	>90% removal with a membrane bioreactor, <0.04 ng/L (includes membrane filtration)
Reverse Osmosis (RO)	More than 90% removal (rejection of bound arsenic and removal of soluble arsenic)	More than 98% removal		
Granular Activated Carbon (GAC)	No removal, removal only when carbon is impregnated with iron	90 % removal	<300 ng/L (precipitation and carbon adsorption) <51 ng/L (GAC)	<800 ng/L Likely requires upstream filtration
Disinfection	--	--	--	--

4.4 Unit Processes Selected

The key conclusion from the literature review was that there is limited, to no evidence, that existing treatment technologies are capable of simultaneously meeting all four of the revised discharge limits for the toxics under consideration. Advanced treatment using RO or GAC is expected to provide the best overall removal of the constituents of concern. It is unclear whether these advanced technologies are able to meet revised effluent limits, however these processes may achieve the best effluent quality of the technologies reviewed. This limitation in the findings is based on a lack of an extensive dataset on treatment removal effectiveness in the technical literature for the constituents of interest at the low levels relevant to the proposed criteria, which

approach the limits of reliable removal performance for the technologies. As Table 4 highlights, certain unit processes are capable of removing a portion, or all, of the removal requirements for each technology. The removal performance for each constituent will vary from facility to facility and require a site-specific, detailed evaluation because the proposed criteria are such low concentrations. In some cases, a facility may only have elevated concentrations of a single constituent of concern identified in this study. In other cases, a discharger may have elevated concentrations of the four constituents identified in this study, as well as others not identified in this study but subject to revised water quality criteria. This effort is intended to describe a planning level concept of what treatment processes are required to comply with discharge limits for all four constituents. Based on the literature review of unit processes above, two different treatment trains were developed for the analysis that are compared against a baseline of secondary treatment as follows:

- Baseline: represents conventional secondary treatment that is most commonly employed nationwide at wastewater treatment plants. A distinguishing feature for this treatment is the short solids residence time (SRT) (<8 days) is intended for removal of BOD with minimal removal for the toxic constituents of concern.
- Advanced Treatment – MF/RO: builds on baseline with the implementation of a longer SRT (>8 days) and the addition of MF and RO. The longer SRT not only removes BOD, but it also has the capacity to remove nutrients and a portion of the constituents of concern. This alternative requires a RO brine management strategy which will be discussed in sub-sections below.
- Advanced Treatment – MF/GAC: this alternative provides a different approach to advanced treatment with MF/RO by using GAC and avoiding the RO reject brine water management concern. Similar to the MF/RO process, this alternative has the longer SRT (>8 days) with the capacity to remove BOD, nutrients, and a portion of the toxic constituents of concern. As a result, the decision was made to develop costs for both advanced treatment options.

A description of each alternative is provided in Table 5. The process flowsheets for each alternative are presented in Figure 3 to Figure 5.

4.4.1 Baseline Treatment Process

A flowsheet of the baseline treatment process is provided in Figure 3. The baseline treatment process assumes the current method of treatment commonly employed by dischargers. For this process, water enters the headworks and undergoes primary treatment, followed by conventional activated sludge (short SRT) and disinfection. The solids wasted in the activated sludge process are thickened, followed by mixing with primary solids prior to entering the anaerobic digestion process for solids stabilization. The digested biosolids are dewatered to produce a cake and hauled off-site. Since the exact process for each interested facility in Washington is unique, this baseline treatment process was used to establish the baseline capital and O&M costs. The baseline costs will be compared against the advanced treatment alternatives to illustrate the magnitude of the increased costs and environmental impacts.

Table 5. Unit Processes Description for Each Alternative

Unit Process	Baseline	Advanced Treatment – MF/RO	Advanced Treatment - GAC
Influent Flow	5 mgd	5 mgd	5 mgd
Chemically Enhanced Primary Treatment (CEPT); Optional	--	• Metal salt addition (alum) upstream of primaries	• Metal salt addition (alum) upstream of primaries
Activated Sludge	• Hydraulic Residence Time (HRT): 6 hrs • Short Solids Residence Time (SRT): <8 days	• Hydraulic Residence Time (HRT): 12 hrs (Requires more tankage than the Baseline) • Long Solids Residence Time (SRT): >8 days (Requires more tankage than the Baseline)	• Hydraulic Residence Time (HRT): 12 hrs (Requires more tankage than the Baseline) • Long Solids Residence Time (SRT): >8 days (Requires more tankage than the Baseline)
Secondary Clarifiers	Hydraulically Limited	Solids Loading Limited (Larger clarifiers than Baseline)	Solids Loading Limited (Larger clarifiers than Baseline)
Microfiltration (MF)	--	Membrane Filtration to Remove Particles and Bacteria	Membrane Filtration to Remove Particles and Bacteria
Reverse Osmosis (RO)	--	Treat 50% of the Flow by RO to Remove Metals and Dissolved Constituents. Sending a portion of flow through the RO and blending it with the balance of plant flows ensures a stable non-corrosive, non-toxic discharge.	--
Reverse Osmosis Brine Reject Mgmt	--	Several Options (All Energy or Land Intensive)	--
Granular Activated Carbon (GAC)	--	--	Removes Dissolved Constituents
Disinfection	Not shown to remove any of the constituents	Not shown to remove any of the constituents	Not shown to remove any of the constituents

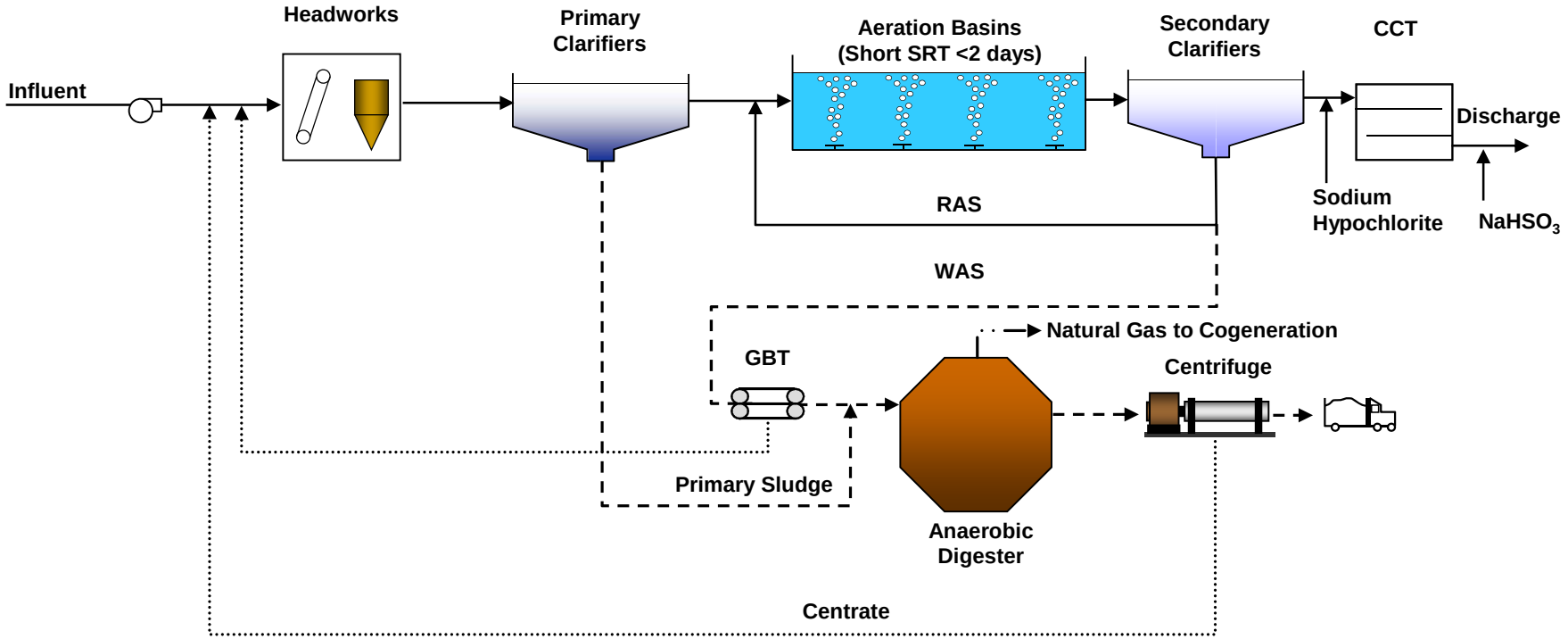

Figure 3. Baseline Flowsheet – Conventional Secondary Treatment

4.4.2 Advanced Treatment – MF/RO Alternative

A flowsheet of the advanced treatment – MF/RO alternative is provided in Figure 4. This alternative builds on the baseline secondary treatment facility, whereby the SRT is increased in the activated sludge process, and MF and RO are added prior to disinfection. The solids treatment train does not change with respect to the baseline. Additionally, a brine management strategy must be considered.

The RO process concentrates contaminants into a smaller volume reject stream. Disposing of the RO reject stream can be a problem because of the potentially large volume of water involved and the concentration of contaminants contained in the brine. For reference, a 5 mgd process wastewater flow might result in 1 mgd of brine reject requiring further management. The primary treatment/handling options for RO reject are as follows:

- Zero liquid discharge
- Surface water discharge
- Ocean discharge
- Haul and discharge to coastal location for ocean discharge
- Sewer discharge
- Deep well injection
- Evaporate in a pond
- Solar pond concentrator

Many of the RO brine reject management options above result in returning the dissolved solids to a “water of the state” such as surface water, groundwater, or marine waters. Past rulings in Washington State have indicated that once pollutants are removed from during treatment they are not to be re-introduced to a water of the state. As a result, technologies with this means for disposal were not considered viable options for management of RO reject water in Washington.

Zero Liquid Discharge

Zero liquid discharge (ZLD) is a treatment process that produces a little or no liquid brine discharge but rather a dried residual salt material. This process improves the water recovery of the RO system by reducing the volume of brine that must be treated and disposed of in some manner. ZLD options include intermediate treatment, thermal-based technologies, pressure driven membrane technologies, electric potential driven membrane technologies, and other alternative technologies.

Summary

There are many techniques which can be used to manage reject brine water associated with RO treatment. The appropriate alternative is primarily governed by geographic and local constraints. A comparison of the various brine management methods and potential costs are provided in Table 6.

Of the listed options, ZLD was considered for this analysis as the most viable approach to RO reject water management. An evaporation pond was used following ZLD. The strength in this combination is ZLD reduces the brine reject volume to treat, which in turn reduces the required evaporation pond footprint. The disadvantage is that evaporation ponds require a substantial amount of physical space which may not be available at existing treatment plant sites. It is also important to recognize that the greenhouse gas (GHG) emissions vary widely for the eight brine management options listed above based on energy and chemical intensity.

Table 6. Brine Disposal Method Relative Cost Comparison

Disposal Method	Description	Relative Capital Cost	Relative O&M Cost	Comments
Zero Liquid Discharge (ZLD)	Further concentrates brine reject for further downstream processing	High	High	This option is preferred as an intermediate step. This rationale is based on the reduction in volume to handle following ZLD. For example, RO reject stream volume is reduced on the order of 50-90%.
Surface Water Discharge	Brine discharge directly to surface water. Requires an NPDES permit.	Lowest	Lowest	Both capital and O&M costs heavily dependent on the distance from brine generation point to discharge. Not an option for nutrient removal.
Ocean Discharge	Discharge through a deep ocean outfall.	Medium	Low	Capital cost depends on location and availability of existing deep water outfall.
Sewer Discharge	Discharge to an existing sewer pipeline for treatment at a wastewater treatment plant.	Low	Low	Both capital and O&M costs heavily dependent on the brine generation point to discharge distance. Higher cost than surface water discharge due to ongoing sewer connection charge. Not an option for wastewater treatment.
Deep Well Injection	Brine is pumped underground to an area that is isolated from drinking water aquifers.	Medium	Medium	Technically sophisticated discharge and monitoring wells required. O&M cost highly variable based on injection pumping energy.
Evaporation Ponds	Large, lined ponds are filled with brine. The water evaporates and a concentrated salt remains.	Low – High	Low	Capital cost highly dependent on the amount and cost of land.
Salinity Gradient Solar Ponds (SGSP)	SGSPs harness solar power from pond to power an evaporative unit.	Low – High	Lowest	Same as evaporation ponds plus added cost of heat exchanger and pumps. Lower O&M cost due to electricity production.
Advanced Thermal Evaporation	Requires a two-step process consisting of a brine concentrator followed by crystallizer	High	Highest	Extremely small footprint, but the energy from H_2O removal is by far the most energy intensive unless waste heat is used.

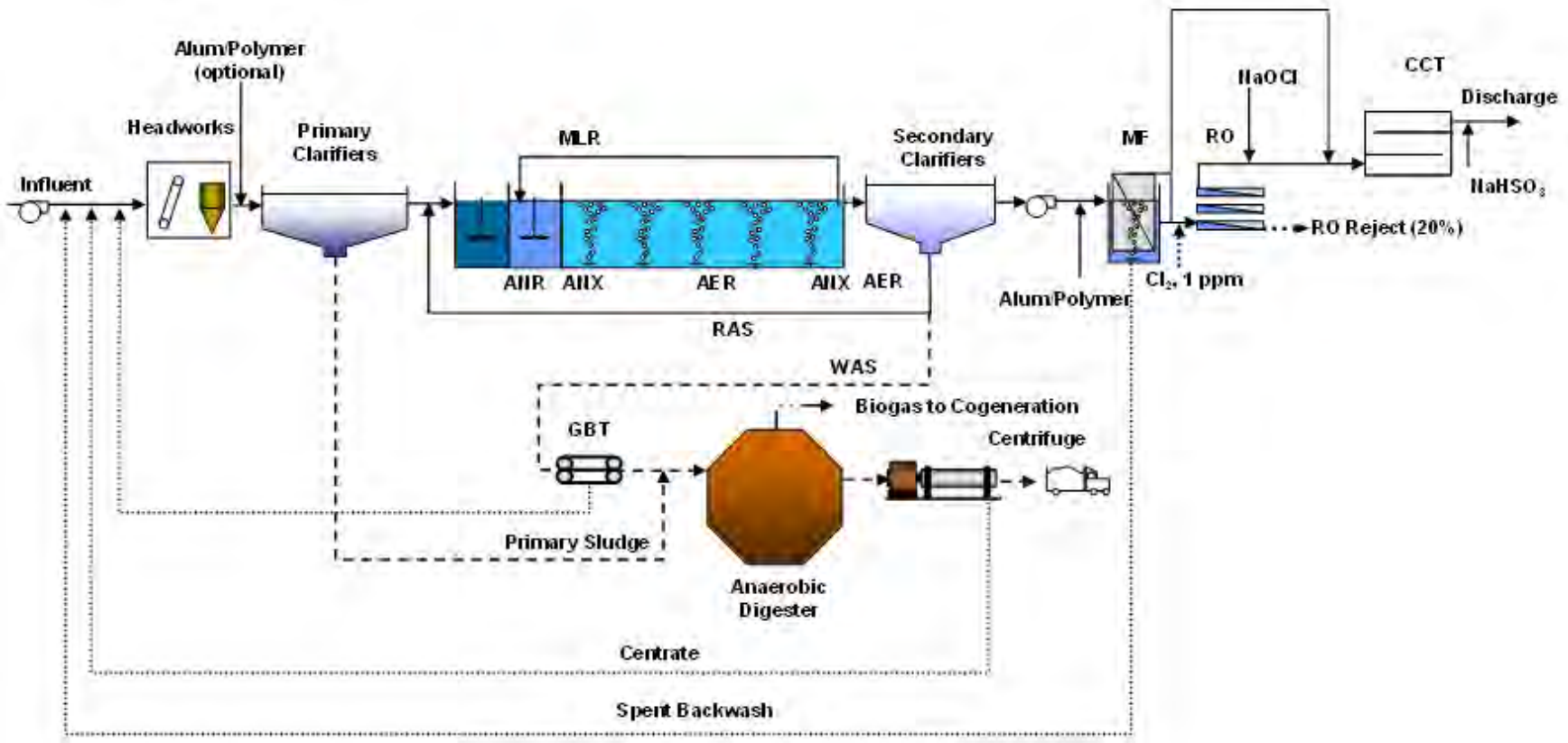

Figure 4. Advanced Treatment Flowsheet – Tertiary Microfiltration and Reverse Osmosis

4.4.3 Advanced Treatment – MF/GAC Alternative

A flowsheet of the advanced treatment – MF/GAC alternative is provided in Figure 5. Following the MF technology, a GAC contactor and media are required.

This alternative was developed as an option that does not require a brine management technology (e.g., ZLD) for comparison to the MF/RO advanced treatment alternative. However, this treatment alternative does require that the GAC be regenerated. A baseline secondary treatment facility can be retrofitted for MF/GAC. If an existing treatment facility has an extended aeration lagoon, the secondary effluent can be fed to the MF/GAC. The longer SRT in the extended aeration lagoon provides all the benefits associated with the long SRT in an activated sludge plant as previously stated:

- Lower BOD/TSS discharge load
- Higher removal of recalcitrant constituents and heavy metals
- Improved water quality and benefit to downstream users
- Less downstream algal growth
- Reduced receiving water dissolved oxygen demand due to ammonia removal
- Reduced ammonia discharge loads, which is toxic to several aquatic species
- Improved water quality for habitat, especially as it relates to biodiversity and eutrophication
- Secondary clarifier effluent more conditioned for filtration and disinfection
- Greater process stability from the anaerobic/anoxic zones serving as a selector

If an existing treatment facility employs a high rate activated sludge process (short SRT) similar to the baseline, it is recommended that the activated sludge process SRT be increased prior to the MF/GAC unit processes. The longer SRT upstream of the MF is preferred to enhance the membrane flux rate, reduce membrane biofouling, increase membrane life, and reduce the chemicals needed for membrane cleaning.

The key technical and operational challenges associated with the tertiary add-on membrane filtration units are as follows:

- The membrane filtration technology is a proven and reliable technology. With over 30 years of experience, it has made the transition in recent years from an emerging technology to a proven and reliable technology.
- Membrane durability dependent on feed water quality. The water quality is individual facility specific.
- Membranes are sensitive to particles, so upstream screening is critical. The newer generations of membranes have technical specifications that require a particular screen size.
- Membrane area requirements based on peak flows as water must pass through the membrane pores. Additionally, membranes struggle with variable hydraulic loading. Flow equalization upstream can greatly reduce the required membrane surface area and provide uniform membrane loading.

- Membrane tanks can exacerbate any foam related issues from the upstream biological process. Foam entrapment in the membrane tank from the upstream process can reduce membrane filtration capacity and in turn result in a plant-wide foam problem.
- Reliable access to the membrane modules is key to operation and maintenance. Once PLC is functionary properly, overall maintenance requirements for sustained operation of the system are relatively modest.
- The membranes go through frequent membrane relaxing or back pulse and a periodic deep chemical clean in place (CIP) process.
- Sizing of membrane filtration facilities governed by hydraulic flux. Municipal wastewaters have flux values that range from about 20 to 40 gallons per square foot per day (gfd) under average annual conditions. The flux associated with industrial applications is wastewater specific.

Following the MF is the activated carbon facilities. There are two kinds of activated carbon used in treating water: powdered activated carbon (PAC) and GAC. PAC is finely-ground, loose carbon that is added to water, mixed for a short period of time, and removed. GAC is larger than PAC, is generally used in beds or tanks that permit higher adsorption and easier process control than PAC allows, and is replaced periodically. PAC is not selective, and therefore, will adsorb all active organic substances making it an impractical solution for a wastewater treatment plant. As a result, GAC was considered for this analysis. The type of GAC (e.g., bituminous and subbituminous coal, wood, walnut shells, lignite or peat), gradation, and adsorption capacity are determined by the size of the largest molecule/ contaminant that is being filtered (AWWA, 1990).

As water flows through the carbon bed, contaminants are captured by the surfaces of the pores until the carbon is no longer able to adsorb new molecules. The concentration of the contaminant in the treated effluent starts to increase. Once the contaminant concentration in the treated water reaches an unacceptable level (called the breakthrough concentration), the carbon is considered "spent" and must be replaced by virgin or reactivated GAC.

The capacity of spent GAC can be restored by thermal reactivation. Some systems have the ability to regenerate GAC on-site, but in general, small systems haul away the spent GAC for off-site regeneration (EPA 1993). For this study, off-site regeneration was assumed.

The basic facilities and their potential unit processes included in this chapter are as follows:

- GAC supply and delivery
- Influent pumping
  - Low head feed pumping
  - High head feed pumping (assumed for this study as we have low limits so require high beds)
- Contactors and backwash facilities
  - Custom gravity GAC contactor
  - Pre-engineered pressure GAC contactor (Used for this study)
  - Backwash pumping
- GAC transport facilities
  - Slurry pumps
  - Eductors (Used for this study)

- Storage facilities
  - Steel tanks
  - Concrete tanks (Used for this study; larger plants would typically select concrete tanks)
- Spent carbon regeneration
  - On-site GAC regeneration
  - Off-Site GAC regeneration

Following the MF is the GAC facility. The GAC contactor provides about a 12-min hydraulic residence time for average annual conditions. The GAC media must be regenerated about twice per year in a furnace. The constituents sorbed to the GAC media are removed during the regeneration process. A typical design has full redundancy and additional storage tankage for spent and virgin GAC. Facilities that use GAC need to decide whether they will regenerate GAC on-site or off-site. Due to challenges associated with receiving air emission permits for new furnaces, it was assumed that off-site regeneration would be evaluated.

The key technical and operational challenges associated with the tertiary add-on GAC units are as follows:

- Nearest vendor to acquire virgin GAC – How frequently can they deliver virgin GAC and what are the hauling costs?
- Contactor selection is typically based on unit cost and flow variation. The concrete contactor is typically more cost effective at higher flows so it was used for this evaluation. The pre-engineered pressure contactor can handle a wider range of flows than a concrete contactor. Additionally, a pressure system requires little maintenance as they are essentially automated
- Periodical contactor backwashing is critical for maintaining the desired hydraulics and control biological growth
- Eductors are preferred over slurry pumps because they have fewer mechanical components. Additionally, the pump with eductors is not in contact with the carbon, which reduces wear.
- Off-site GAC regeneration seems more likely due to the challenges with obtaining an air emissions permit.

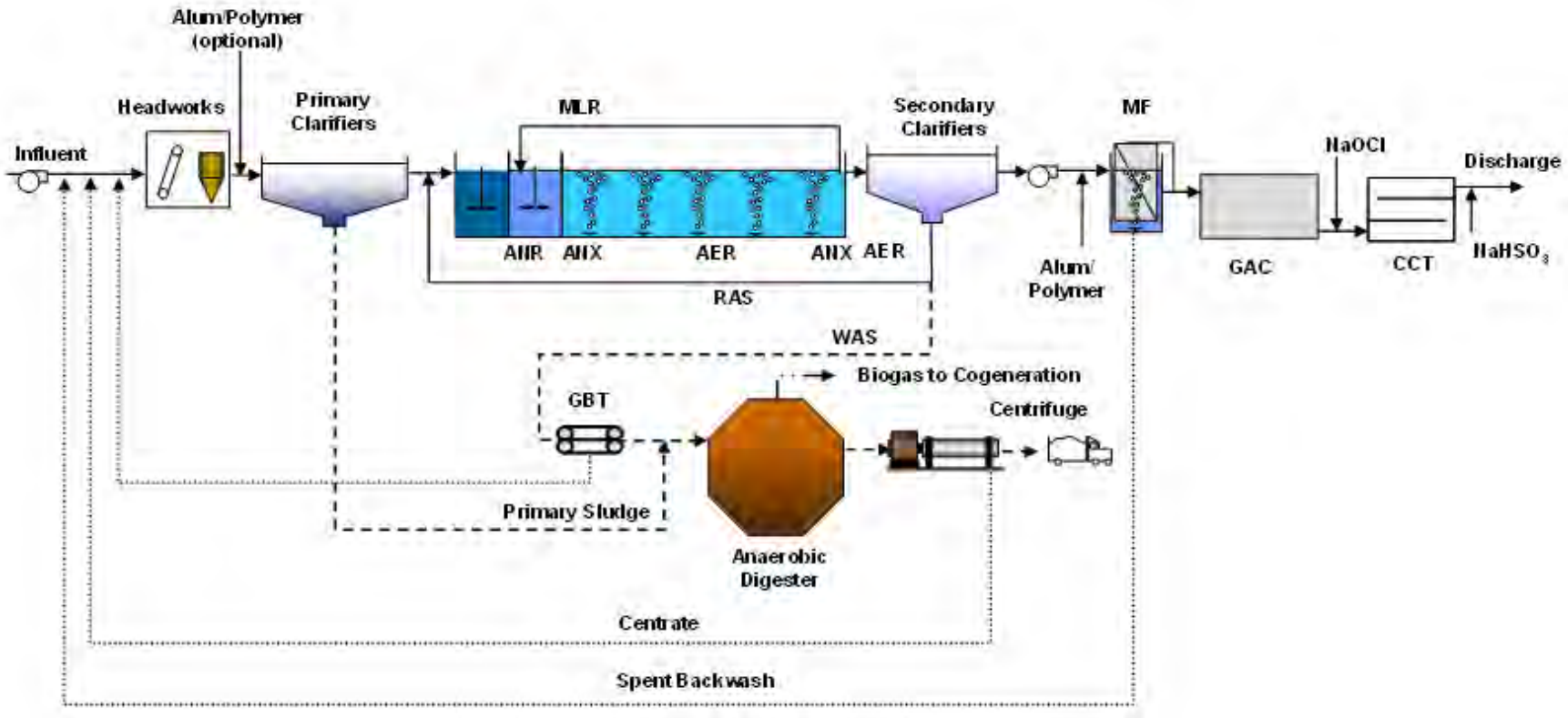

Figure 5. Advanced Treatment Flowsheet – Tertiary Microfiltration and Granular Activated Carbon

4.5 Steady-State Mass Balance

HDR used its steady-state mass balance program to calculate the flows and loads within the candidate advanced treatment processes as a means to size facilities. The design of wastewater treatment facilities are generally governed by steady-state mass balances. For a steady-state mass balance, the conservation of mass is calculated throughout the entire wastewater treatment facility for defined inputs. Dynamic mass balance programs exist for designing wastewater facilities, but for a planning level study such as this, a steady state mass balance program is adequate. A dynamic program is generally used for detailed design and is site-specific with associated requirements for more detailed wastewater characterization.

The set of model equations used to perform a steady-state mass balance are referred to as the model. The model equations provide a mathematical description of various wastewater treatment processes, such as an activated sludge process, that can be used to predict unit performance. The program relies on equations for each unit process to determine the flow, load, and concentration entering and leaving each unit process.

An example of how the model calculates the flow, load, and concentration for primary clarifiers is provided below. The steady-state mass balance equation for primary clarifiers has a single input and two outputs as shown in the simplified Figure 6. The primary clarifier feed can exit the primary clarifiers as either effluent or sludge. Solids not removed across the primaries leave as primary effluent, whereas solids captured leave as primary sludge. Scum is not accounted for.

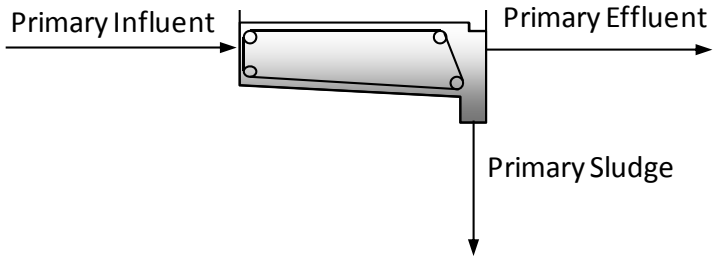

Figure 6. Primary Clarifier Inputs/Outputs

The mass balance calculation requires the following input:

- Solids removal percentage across the primaries (based on average industry accepted performance)
- Primary solids thickness (i.e., percent solids) (based on average industry accepted performance)

The steady-state mass balance program provides a reasonable first estimate for the process performance, and an accurate measure of the flows and mass balances at various points throughout the plant. The mass balance results were used for sizing the facility needs for each alternative. A listing of the unit process sizing criterion for each unit process is provided in Appendix A. By listing the unit process sizing criteria, a third-party user could redo the analysis and end up with comparable results. The key sizing criteria that differ between the baseline and treatment alternatives are as follows:

- Aeration basin mixed liquor is greater for the advanced treatment alternatives which in turn requires a larger volume
- The secondary clarifiers are sized based on hydraulic loading for the baseline versus solids loading for the advanced treatment alternatives

- The MF/GAC and MF/RO sizing is only required for the respective advanced treatment alternatives.

4.6 Adverse Environmental Impacts Associated with Advanced Treatment Technologies

The transition from the baseline (conventional secondary treatment) to either advanced treatment alternatives has some environmental impacts that merit consideration, including the following:

- Land area for additional system components (which for constrained facility sites, may necessitate land acquisition and encroachment into neighboring properties with associated issues and challenges, etc.).
- Increased energy use and atmospheric emissions of greenhouse gases and criteria air contaminants associated with power generation to meet new pumping requirements across the membrane filter systems (MF and RO) and GAC.
- Increased chemical demand associated with membrane filters (MF and RO).
- Energy and atmospheric emissions associated with granulated charcoal regeneration.
- RO brine reject disposal. The zero liquid discharge systems are energy intensive energy and increase atmospheric emissions as a consequence of the electrical power generation required for removing water content from brine reject.
- Increase in sludge generation while transitioning from the baseline to the advanced treatment alternatives. There will be additional sludge captured with the chemical addition to the primaries and membrane filters (MF and RO). Additionally, the GAC units will capture more solids.
- Benefits to receiving water quality by transitioning from a short SRT (<2 days) in the baseline to a long SRT (>8 days) for the advanced treatment alternatives (as previously stated):
    - Lower BOD/TSS discharge load
    - Higher removal of recalcitrant constituents and heavy metals
    - Improved water quality and benefit to downstream users
    - Reduced nutrient loadings to receiving waters and lower algal growth potential
    - Reduced receiving water dissolved oxygen demand due to ammonia removal
    - Reduced ammonia discharge loads, which is toxic to aquatic species
    - Improved water quality for habitat, especially as it relates to biodiversity and eutrophication
    - Secondary clarifier effluent better conditioned for subsequent filtration and disinfection
    - Greater process stability from the anaerobic/anoxic zones serving as a biological selectors

HDR calculated GHG emissions for the baseline and advanced treatment alternatives. The use of GHG emissions is a tool to normalize the role of energy, chemicals, biosolids hauling, and fugitive emissions (e.g., methane) in a single unit. The mass balance results were used to quantify energy demand and the corresponding GHG emissions for each alterative. Energy

demand was estimated from preliminary process calculations. A listing of the energy demand for each process stream, the daily energy demand, and the unit energy demand is provided in Table 7. The advanced treatment options range from 2.3 to 4.1 times greater than the baseline. This large increase in energy demand is attributed to the energy required to pass water through the membrane barriers and/or the granular activated carbon. Additionally, there is energy required to handle the constituents removed as either regenerating the GAC or handling the RO brine reject water. This additional energy required to treat the removed constituents is presented in Table 7.

Table 7. Energy Breakdown for Each Alternative (5 mgd design flow)

Parameter	Units	Baseline	Advanced Treatment – MF/GAC	Advanced Treatment – MF/RO
Daily Liquid Stream Energy Demand	MWh/d	11.6	23.8	40.8
Daily Solids Stream Energy Demand	MWh/d	-1.6	-1.1	-1.1
Daily Energy Demand	MWh/d	10.0	22.7	39.7
Unit Energy Demand	kWh/MG Treated	2,000	4,500	7,900

MWh/d = megawatt hours per day
kWh/MG = kilowatt hours per million gallons

Details on the assumptions used to convert between energy demand, chemical demand and production, as well as biologically-mediated gases (i.e., CH4 and N2O) and GHG emissions are provided in Appendix B.

A plot of the GHG emissions for each alternative is shown in Figure 7. The GHG emissions increase from the baseline to the two advanced treatment alternatives. The GHG emissions increase about 50 percent with respect to baseline when MF/GAC is used and the GHG emissions increase over 100 percent with respect to baseline with the MF/RO advanced treatment alternative.

The MF/GAC energy demand would be larger if GAC regeneration was performed on-site. The GHG emissions do not include the energy or air emissions that result from off-site GAC regeneration. Only the hauling associated with moving spent GAC is included. The energy associated with operating the furnace would exceed the GHG emissions from hauling spent GAC.

The zero liquid discharge in the MF/RO alternative alone is comparable to the Baseline. This contribution to increased GHG emissions by zero liquid discharge brine system highlights the importance of the challenges associated with managing brine reject.

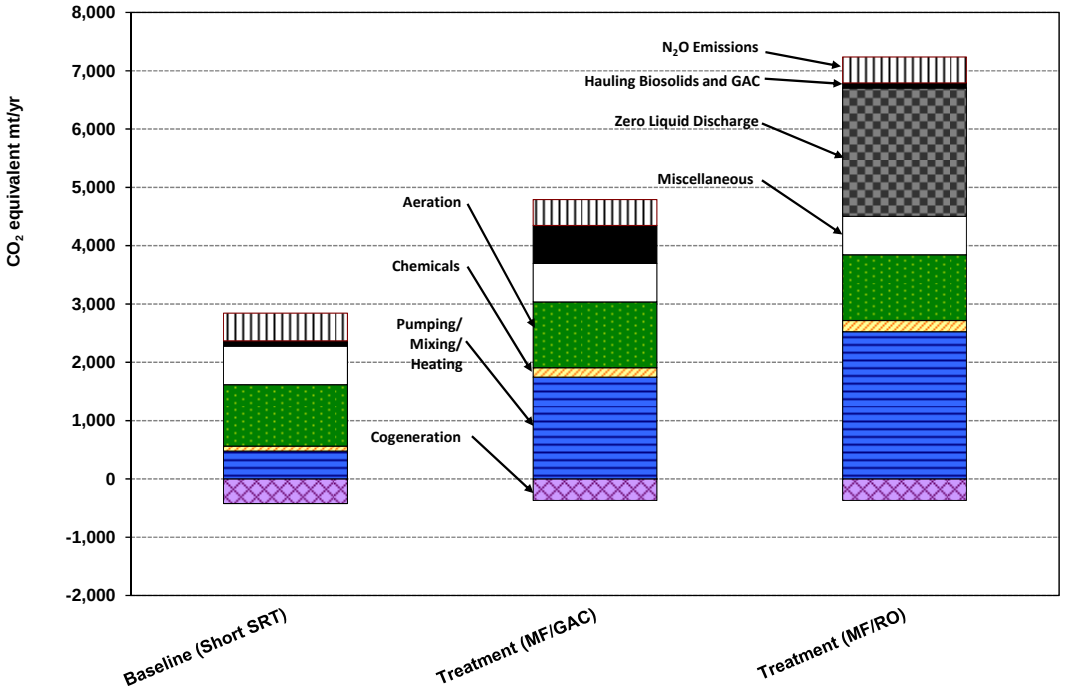

Figure 7. Greenhouse Gas Emissions for Each Alternative

The use of GHG emissions as a measure of sustainability does not constitute a complete comparison between the baseline and advanced treatment alternatives. Rather, it is one metric that captures the impacts of energy, chemical demand and production, as well as biologically-mediated gases (i.e., CH_4 and N_2O). The other environmental impacts of advanced treatment summarized in the list above should also be considered in decision making beyond cost analysis.

4.7 Costs

Total project costs along with the operations and maintenance costs were developed for each advanced treatment alternative for a comparison with baseline secondary treatment.

4.7.1 Approach

The cost estimates presented in this report are planning level opinions of probable construction costs for a nominal 5 mgd treatment plant design flow representing a typical facility without site specific details about local wastewater characteristics, physical site constraints, existing infrastructure, etc. The cost estimates are based on wastewater industry cost references, technical studies, actual project cost histories, and professional experience. The costs presented in this report are considered planning level estimates. A more detailed development of the advanced treatment process alternatives and site specific information would be required to further refine the cost estimates. Commonly this is accomplished in the preliminary design phase of project development for specific facilities following planning.

The cost opinion includes a range of costs associated with the level of detail used in this analysis. Cost opinions based on preliminary engineering can be expected to follow the Association for the Advancement of Cost Engineering (AACE International) Recommended Practice No. 17R-97 Cost Estimate Classification System estimate Class 4. A Class 4 estimate is based upon a 5 to 10 percent project definition and has an expected accuracy range of -30 to +50 percent and typical end usage of budget authorization and cost control. It is considered an

"order-of-magnitude estimate." The life-cycle costs were prepared using the net present value (NPV) method.

The cost associated for each new unit process is based on a unit variable, such as required footprint, volume, demand (e.g., lb O_2/hr), and others. This approach is consistent with the approach developed for the EPA document titled "Estimating Water Treatment Costs: Volume 2-Cost Curves Applicable to 1 to 200 mgd Treatment Plants" dated August 1979. The approach has been updated since 1979 to account for inflation and competition, but the philosophy for estimating costs for unit processes has not changed. For example, the aeration system sizing/cost is governed by the maximum month airflow demand. Additionally, the cost associated constructing an aeration basin is based on the volume. The cost considers economies of scale.

The O&M cost estimates were calculated from preliminary process calculations. The operations cost includes energy and chemical demand. For example, a chemical dose was assumed based on industry accepted dosing rates and the corresponding annual chemical cost for that particular chemical was accounted for. The maintenance values only considered replacement equipment, specifically membrane replacement for the Advanced Treatment Alternatives.

4.7.2 Unit Cost Values

The life-cycle cost evaluation was based on using the economic assumptions shown in Table 8. The chemical costs were based on actual values from other projects. To perform detailed cost evaluations per industry, each selected technology would need to be laid out on their respective site plan based on the location of the existing piping, channels, and other necessary facilities.

Table 8. Economic Evaluation Variables

Item	Value
Nominal Discount Rate	5%
Inflation Rate:	
General	3.5%
Labor	3.5%
Energy	3.5%
Chemical	3.5%
Base Year	2013
Project Life	25 years
Energy	$0.06/kWh
Natural Gas	$0.60/therm
Chemicals:	
Alum	$1.1/gal
Polymer	$1.5/gal
Hypochlorite	$1.5/gal
Salt	$0.125/lb
Antiscalant	$12.5/lb
Acid	$0.35/lb
Deionized Water	$3.75/1,000 gal
Hauling:	

Table 8. Economic Evaluation Variables

Item	Value
Biosolids Hauling Distance	100 miles (one way)
Biosolids Truck Volume	6,000 gal/truck
Biosolids Truck Hauling	$250/truck trip
GAC Regeneration Hauling Distance	250 miles (round trip)
GAC Regeneration Truck Volume	$20,000 lb GAC/truck
GAC Regeneration Truck Hauling	Included in cost of Virgin GAC

kWh= kilowatt hours; lbs=pounds; GAC=granulated activated carbon; gal=gallon

4.7.3 Net Present Value of Total Project Costs and Operations and Maintenance Cost in 2013 Dollars

An estimate of the net present value for the baseline treatment process and the incremental cost to implement the advanced treatment alternatives is shown in Table 9. The cost for the existing baseline treatment process was estimated based on new construction for the entire conventional secondary treatment process (Figure 3). The incremental cost to expand from existing baseline secondary treatment to advanced treatment was calculated by taking the difference between the baseline and the advanced treatment alternatives. These values serve as a benchmark for understanding the prospective cost for constructing advanced treatment at the planning level of process development.

Table 9. Treatment Technology Total Project Costs in 2013 Dollars for a 5 mgd Facility

Alternative	Total Construction Cost, 2013 dollars ($ Million)	O&M Net Present Value, 2013 dollars ($ Million)*	Total Net Present Value, 2013 dollars ($ Million)	NPV Unit Cost, 2013 dollars ($/gpd)
Baseline (Conventional Secondary Treatment)*	59 - 127	5 - 11	65 – 138	13 - 28
Advanced Treatment – MF/RO**	108 - 231	31 - 67	139 - 298	28 - 60
Advanced Treatment – MF/GAC	131 - 280	50 - 108	181 - 388	36 - 78
Incremental Increase to Advanced Treatment MF/RO	48 - 104	26 - 56	75 - 160	15 - 32
Incremental Increase to Advanced Treatment MF/GAC	71 - 153	45 - 97	117 - 250	23 - 50

* The additional cost to increase the SRT to upwards of 30-days is about $12 - 20 million additional dollars in total project cost for a 5 mgd design flow

** Assumes zero liquid discharge for RO brine management, followed by evaporation ponds. Other options are available as listed in Section 4.4.2.

O&M=operations and maintenance; MF/RO=membrane filtration/reverse osmosis; MF/GAC=membrane filtration/granulated activated carbon; gpd=gallons per day

4.7.4 Unit Cost Assessment

Costs presented above are based on a treatment capacity of 5.0 mgd, however, existing treatment facilities range dramatically across Washington in size and flow treated. Table 9 indicates that the unit capital cost for baseline conventional secondary treatment for 5.0 mgd ranges between $13 to 28 per gallon per day of treatment capacity. The unit cost for the advanced treatment alternatives increases the range from the low $20s to upper $70s on a per-gallon per-day of capacity. The increase in cost for the advanced treatment alternatives is discussed in the sub-sections below.

Advanced Treatment MF/RO

The advanced treatment MF/RO alternative has a total present worth unit cost range of $28 to $60 million in per gallon per day of capacity. This translates to an incremental cost increase with respect to the baseline of $15 to $32 million dollars in per gallon per day treatment capacity. The key differences in cost between the baseline and the advanced treatment MF/RO are as follows:

- Larger aeration basins than the baseline to account for the longer SRT (<8 days versus >8 days).
- Additional pumping stations to pass water through the membrane facilities (MF and RO). These are based on peak flows.
- Membrane facilities (MF and RO; equipment, tanks chemical feed facilities, pumping, etc.) and replacement membrane equipment.
- Additional energy and chemical demand to operate the membrane facilities (MF and RO) and GAC.
- Zero liquid discharge facilities to further concentrate the brine reject.
- Zero liquid discharge facilities are energy/chemically intensive and they require membrane replacement every few years due to the brine reject water quality.
- An evaporation pond to handle the brine reject that has undergone further concentration by zero liquid discharge.

The advanced treatment MF/RO assumes that 100 percent of the flow is treated by MF, followed by 50 percent of the flow treated with RO. Sending a portion of flow through the RO and blending it with the balance of plant flows ensures a stable water to discharge. The RO brine reject (about 1.0 mgd) undergoes ZLD pre-treatment that further concentrates the brine reject to about 0.1-0.5 mgd. The recovery for both RO and ZLD processes is highly dependent on water quality (e.g., silicate levels).

ZLD technologies are effective at concentrating brine reject, but it comes at a substantial cost ($17.5 per gallon per day of ZLD treatment capacity of brine reject). The zero liquid discharge estimate was similar in approach to the demonstration study by Burbano and Brandhuber (2012) for La Junta, Colorado. The ability to further concentrate brine reject was critical from a management standpoint. Although 8 different options were presented for managing brine reject in Section 4.4.2, none of them is an attractive approach for handling brine reject. ZLD provides a viable pre-treatment step that requires subsequent downstream treatment. Evaporation ponds following ZLD were used for this study. Without ZLD, the footprint would be 3-5 times greater.

Roughly 30 acres of evaporation ponds, or more, may be required to handle the ZLD concentrate, depending upon concentrator effectiveness, local climate conditions, residuals

accumulation, residual removal, etc. Precipitation throughout Washington is highly variable which can greatly influence evaporation pond footprint. The approach for costing the evaporation pond was in accordance with Mickley et al. (2006) and the cost was about $2.6 million.

Recent discussions with an industry installing evaporation ponds revealed that they will use mechanical evaporators to enhance evaporation rates. The use of mechanical evaporators was not included in this study, but merits consideration if a facility is performing a preliminary design that involves evaporation ponds. The mechanical evaporators have both a capital costs and annual energy costs.

Advanced Treatment MF/GAC

The advanced treatment MF/GAC alternative has a total present worth unit cost range of $36 to $78 million in per gallon per day capacity. This translates to an incremental cost increase with respect to the baseline of $23 to $50 million dollars on a per gallon per day of treatment capacity basis. The key differences in cost between the baseline and the advanced treatment MF/GAC are as follows:

- Larger aeration basins than the baseline to account for the longer SRT (<8 days versus >8 days).
- Additional pumping stations to pass water through the MF membrane and GAC facilities. These are based on peak flows.
- GAC facilities (equipment, contact tanks, pumping, GAC media, etc.)
- Additional energy to feed and backwash the GAC facilities.
- GAC media replacement was the largest contributor of any of the costs.
- Additional hauling and fees to regenerate GAC off-site.

The advanced treatment MF/GAC assumes that 100 percent of the flow is treated by MF, followed by 100 percent of the flow treated with GAC. The GAC technology is an established technology. The costing approach was in accordance with EPA guidelines developed in 1998.

The critical issue while costing the GAC technology is whether a GAC vendor/regeneration facility is located within the region. On-site regeneration is an established technology with a furnace.

However, there are several concerns as listed in Section 4.4.3:

- Ability to obtain an air emissions permit
- Additional equipment to operate and maintain
- Energy and air emissions to operate a furnace on-site
- Operational planning to ensure that furnace is operating 90-95 percent of the time. Otherwise, operations is constantly starting/stopping the furnace which is energy intensive and deleterious to equipment
- If not operated properly, the facility has the potential to create hazardous/toxic waste to be disposed

If located within a couple hundred miles, off-site regeneration is preferred. For this study, off-site regeneration was assumed with a 250-mile (one-way) distance to the nearest vendor that can provide virgin GAC and a regeneration facility.

Incremental Treatment Cost

The difference in costs between the baseline and the advanced treatment alternatives is listed in Table 10. The incremental cost to retrofit the baseline facility to the advanced treatment was calculated by taking the difference between the two alternatives. These values should serve as a planning level benchmark for understanding the potential cost for retrofitting a particular facility. The incremental cost is unique to a particular facility. Several reasons for the wide range in cost in retrofitting a baseline facility to advanced treatment are summarized as follows:

- Physical plant site constraints. A particular treatment technology may or may not fit within the constrained particular plant site. A more expensive technology solution that is more compact may be required. Alternately, land acquisition may be necessary to enlarge a plant site to allow the addition of advanced treatment facilities. An example of the former is stacking treatment processes vertically to account for footprint constraints. This is an additional financial burden that would not be captured in the incremental costs presented in Table 10.
- Yard piping. Site specific conditions may prevent the most efficient layout and piping arrangement for an individual facility. This could lead to additional piping and pumping to convey the wastewater through the plant. This is an additional financial burden that would not be captured in the incremental costs presented in Table 10.
- Pumping stations. Each facility has unique hydraulic challenges that might require additional pumping stations not captured in this planning level analysis. This is an additional financial burden that would not be captured in the incremental costs presented in Table 10.

A cursory unit cost assessment was completed to evaluate how costs would compare for facilities with lower (0.5 mgd) and higher capacity (25 mgd), as presented in Table 10. Capital costs were also evaluated for a 0.5 mgd and 25 mgd facility using non-linear scaling equations with scaling exponents. The unit capital cost for baseline conventional secondary treatment for 0.5 mgd and 25 mgd is approximately $44 and $10 per gallon per day of treatment capacity, respectively. The incremental unit costs to implement an advanced treatment retrofit for 0.5 mgd would range between $30 to $96 per gallon per day of treatment capacity and would be site and discharger specific. The incremental unit costs to implement an advanced treatment retrofit for 25 mgd would range between $10 to 35 per gallon per day of treatment capacity and would be site and discharger specific. The larger flow, 25 mgd, is not as expensive on a per gallon per day of treatment capacity. This discrepancy for the 0.5 and 25 mgd cost per gallon per day of treatment capacity is attributed to economies of scale. Cost curve comparisons (potential total construction cost and total net present value) for the baseline and the two tertiary treatment options (MF/RO and MF/GAC) are shown in Figure 8 and Figure 9 between the flows of 0.5 and 25 mgd. It is important to note that while the economies of scale suggest lower incremental costs for the larger size facilities, some aspects of the advanced treatment processes may become infeasible at larger capacities due to factors such as physical space limitations and the large size requirements for components such as RO reject brine management.

Table 10. Treatment Technology Total Project Costs in 2013 Dollars for a 0.5 mgd Facility and a 25 mgd Facility

Alternative	Total Construction Cost, 2013 dollars ($ Million)	O&M Net Present Value, 2013 dollars ($ Million)*	Total Net Present Value, 2013 dollars ($ Million)	NPV Unit Cost, 2013 dollars ($/gpd)
0.5 mgd:				
Baseline (Conventional Secondary Treatment)	15 - 32	0.5 - 1.1	15 - 33	31 - 66
Advanced Treatment – MF/RO**	27 - 58	3.2 - 6.8	30 - 65	60 - 130
Advanced Treatment – MF/GAC	33 - 70	5 - 10.8	38 - 81	76 - 162
Incremental Increase to Advanced Treatment MF/RO	12 - 26	2.7 - 5.7	15 - 32	30 - 64
Incremental Increase to Advanced Treatment MF/GAC	18 - 38	4.6 - 9.8	22 - 48	45 - 96
25 mgd:				
Baseline (Conventional Secondary Treatment)	156 - 335	25 - 54	182 - 389	7 - 16
Advanced Treatment – MF/RO**	283 - 606	157 - 336	440 - 942	18 - 38
Advanced Treatment – MF/GAC	343 - 735	252 - 541	595 - 1276	24 - 51
Incremental Increase to Advanced Treatment MF/RO	127 - 272	131 - 281	258 - 553	10 - 22
Incremental Increase to Advanced Treatment MF/GAC	187 - 401	226.9 - 486	414 - 887	17 - 35

* Does not include the cost for labor.
** Assumes zero liquid discharge for RO brine management, followed by evaporation ponds. Other options are available as listed in Section 4.4.2.
MF/RO=membrane filtration/reverse osmosis
MF/GAC=membrane filtration/granulated activated carbon
O&M=operations and maintenance
gpd=gallons per day

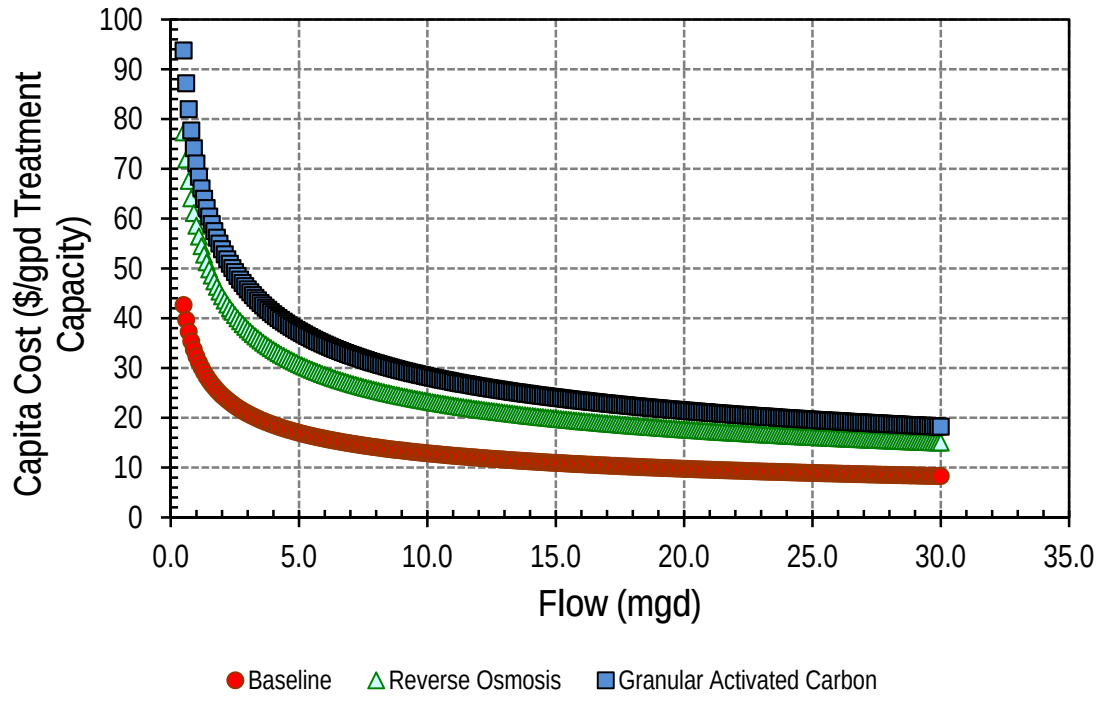

Figure 8: Capital Cost Curve Comparison for Baseline Treatment, MF/RO, and MF/GAC

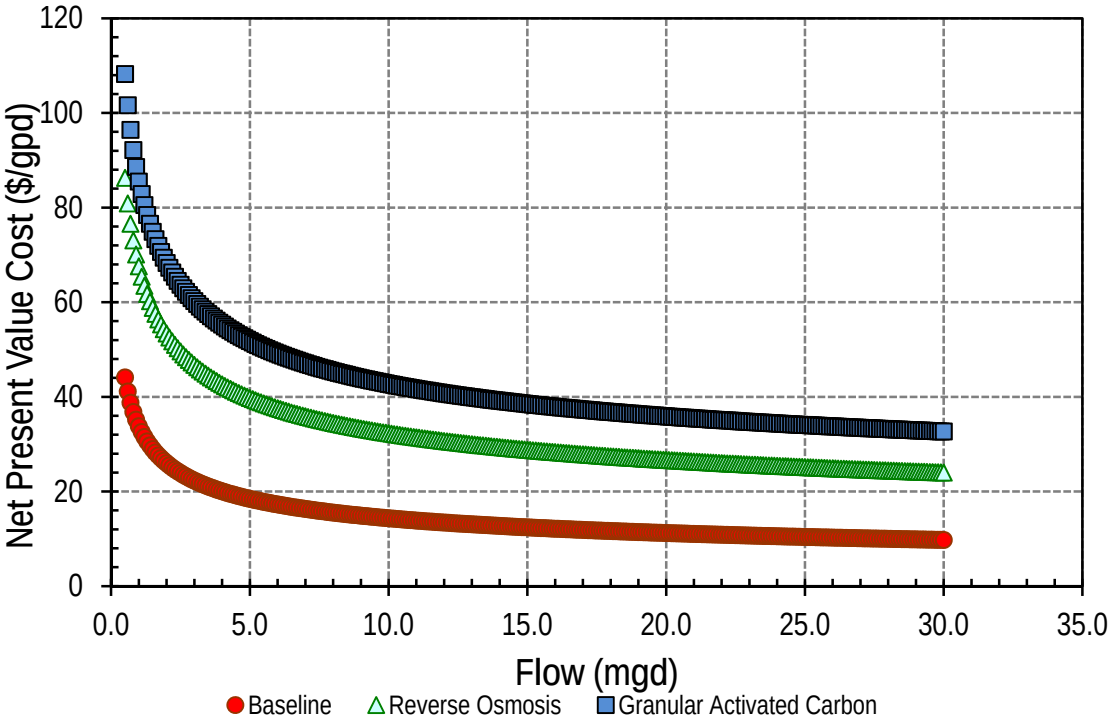

Figure 9: NPV Cost Curve Comparison for Baseline Treatment, MF/RO, and MF/GAC

4.8 Pollutant Mass Removal

An estimate of the projected load removal for the four constituents of concern was developed and is presented in Table 11. The current secondary effluent and advanced treatment effluent data is based on the only available data to HDR and is from municipal treatment plant facilities. Data is not available for advanced treatment facilities such as MF/RO or MF/GAC. Due to this lack of data, advanced treatment using MF/RO or MF/GAC was assumed to remove an additional zero to 90 percent of the constituents presented resulting in the range presented in Table 11. It is critical to note these estimates are based on limited data and are presented here simply for calculating mass removals. Current secondary effluent for industrial facilities would likely be greater than the data presented here and as a result, the projected effluent quality for industrial facilities would likely be higher as well. Based on the limited actual data from municipal treatment facilities, Table 11 indicates that mercury and BAP effluent limits may potentially be met using advanced treatment at facilities with similar existing secondary effluent quality.

Table 11. Pollutant Mass Removal by Contaminant for a 5 mgd Facility

Component	PCBs	Mercury	Arsenic	BAP
Required HHWQC based Effluent Quality (µg/L)	0.0000064	0.005	0.018	0.0013
Current Secondary Effluent Concentration (µg/L)*	0.0015	0.025	7.5	0.00031
Projected Effluent Quality (µg/L) from Advanced Treatment (MF/RO or MF/GAC)*	0.000041 – 0.00041	0.00012 – 0.0012	0.38 – 3.8	0.000029 - 0.00029
Mass Removed (mg/d)**	21 - 28	451 - 471	71,000 – 135,000	0.4 – 5.0
Mass Removed (lb/d)**	0.000045 – 0.000061	0.00099 – 0.0010	0.16 – 0.30	0.0000010 – 0.0000012

* Based on or estimated for actual treatment plant data from municipal facilities. Data sets are limited and current secondary effluent for industrial facilities would likely be greater than the data presented here.
** 1 lb = 454,000 mg
HHWQC=human health-based water quality criteria
MF/RO=membrane filtration/reverse osmosis
MF/GAC=membrane filtration/granulated activated carbon
µg/L=micrograms per liter
mg/d=milligrams per day
lb/d=pounds per day

Unit costs were developed based on required mass removal from a 5 mgd facility for each of the four constituents of concern to reduce discharges from current secondary effluent quality to the assumed required effluent quality (HHWQC). It important to note that this study concludes it is unclear if existing technology can meet the required effluent quality, however, the information presented in Table 12 assumes HHWQC would be met for developing unit costs. The unit costs are expressed as dollars in NPV (over a 25 year period) per pound of constituent removed over the same 25 year period using advanced treatment with MF/RO. The current secondary effluent quality data presented are based on typical secondary effluent quality expected for a municipal/industrial discharger. Table 12 suggests unit costs are most significant in meeting the PCB, mercury, and PAH required effluent quality.

Table 12. Unit Cost by Contaminant for a 5 mgd Facility Implementing Advanced Treatment using MF/RO

Component	PCBs	Mercury	Arsenic	PAHs
Required HHWQC based Effluent Quality (µg/L)	0.0000064	0.005	0.018	0.0013
Current Secondary Effluent Concentration (µg/L)*	0.002	0.025	7.5	0.006
Total Mass Removed (lbs) over 25-year Period	0.76	7.6	2,800	1.8
Unit Cost (NPV per total mass removed in pounds over 25 years)	$290,000,000	$29,000,000	$77,000	$120,000,000

*Derived from data presented in Table 3.
**Based on assumed 25-year NPV of $219,000,000 (average of the range presented in Table 10) and advanced treatment using MF/RO.
NPV=net present value
HHWQC=human health-based water quality criteria
µg/l=micrograms per liter

4.9 Sensitivity Analysis

The ability of dischargers to meet a HHWQC one order of magnitude less stringent (than HHWQC presented in Table 3 and used in this report) was considered. The same advanced treatment technologies using MF/RO or MF/GAC would still be applied to meet revised effluent quality one order-of-magnitude less stringent despite still not being able to meet less stringent effluent limits. As a result, this less stringent effluent quality would not impact costs. Based on available data, it appears the mercury and BAP limits would be met at a less stringent HHWQC. PCB effluent quality could potentially be met if advanced treatment with RO or GAC performed at the upper range of their projected treatment efficiency. It does not appear the less stringent arsenic HHWQC would be met with advanced treatment. It is important to note that a discharger's ability to meet these less stringent limits depends on existing secondary effluent characteristics and is facility specific. Facilities with higher secondary effluent constituent concentrations will have greater difficulty meeting HHWQC.

5.0 Summary and Conclusions

This study evaluated treatment technologies potentially capable of meeting revised effluent discharge limits associated with revised HHWQC. HDR completed a literature review of potential technologies and engineering review of their capabilities to evaluate and screen treatment methods for meeting revised effluent limits for four constituents of concern: arsenic, BAP, mercury, and PCBs. HDR selected two alternatives to compare against a baseline, including enhanced secondary treatment, enhanced secondary treatment with MF/RO, and enhanced secondary treatment with MF/GAC. HDR developed capital costs, operating costs, and a NPV for each alternative, including the incremental cost to implement from an existing secondary treatment facility.

The following conclusions can be made from this study.

- Revised HHWQC based on state of Oregon HHWQC (2001) and EPA "National Recommended Water Quality Criteria" will result in very low water quality criteria for toxic constituents.
- There are limited "proven" technologies available for dischargers to meet required effluent quality limits that would be derived from revised HHWQC.
    - Current secondary wastewater treatment facilities provide high degrees of removal for toxic constituents; however, they will not be capable of compliance with water quality-based NPDES permit effluent limits derived from revised HHWQC.
    - Advanced treatment technologies have been investigated and candidate process trains have been conceptualized for toxics removal.
        - Advanced wastewater treatment technologies may enhance toxics removal rates, however they will not be capable of compliance with HHWQC based effluent limits for PCBs. The lowest levels achieved based on the literature review were between <0.00001 and 0.00004 µg/L, as compared to a HHWQC of 0.0000064 µg/L.
        - Based on very limited performance data for arsenic and mercury from advanced treatment information available in the technical literature, compliance with revised criteria may or may not be possible, depending upon site specific circumstances.
            - Compliance with a HHWQC for arsenic of 0.018 µg/L appears unlikely. Most treatment technology performance information available in the literature is based on drinking water treatment applications targeting a much higher SDWA MCL of 10 µg/L.
            - Compliance with a HHWQC for mercury of 0.005 µg/L appears to be potentially attainable on an average basis but perhaps not if effluent limits are structured on a maximum monthly, weekly or daily basis. Some secondary treatment facilities attain average effluent mercury levels of 0.009 to 0.066 µg/L. Some treatment facilities with effluent filters attain average effluent mercury levels of 0.002 to 0.010 µg/L. Additional advanced treatment processes are expected to enhance these removal rates, but little mercury performance data is available for a definitive assessment.
        - Little information is available to assess the potential for advanced technologies to comply with revised benzo(a)pyrene criteria. A municipal wastewater treatment plant study reported both influent and effluent BAP concentrations less than the HHWQC of 0.0013 ug/L (Ecology, 2010).

  - Some technologies may be effective at treating identified constituents of concern to meet revised limits while others may not. It is therefore even more challenging to identify a technology that can meet all constituent limits simultaneously.
  - A HHWQC that is one order-of-magnitude less stringent could likely be met for mercury and PAHs however it appears PCB and arsenic limits would not be met.
- Advanced treatment processes incur significant capital and operating costs.
  - Advanced treatment process to remove additional arsenic, benzo(a)pyrene, mercury, and PCBs would combine enhancements to secondary treatment with microfiltration membranes, reverse osmosis, and granular activated carbon and increase the estimated capital cost of treatment from $17 to $29 in dollars per gallon per day of capacity (based on a 5.0 mgd facility).
  - The annual operation and maintenance costs for the advanced treatment process train will be substantially higher (approximately $5 million - $15 million increase for a 5.0 mgd capacity facility) than the current secondary treatment level.
- Implementation of additional treatment will result in additional collateral impacts.
  - High energy consumption.
  - Increased greenhouse gas emissions.
  - Increase in solids production from chemical addition to the primaries. Additionally, the membrane and GAC facilities will capture more solids that require handling.
  - Increased physical space requirements at treatment plant sites for advanced treatment facilities and residuals management including reverse osmosis reject brine processing.
- It appears advanced treatment technology alone cannot meet all revised water quality limits and implementation tools are necessary for discharger compliance.
  - Implementation flexibility will be necessary to reconcile the difference between the capabilities of treatment processes and the potential for HHWQC driven water quality based effluent limits to be lower than attainable with technology

6.0 References

Ahn, J.-H., Kim, S, Park, H., Rahm, B., Pagilla, K., Chandran, K. 2010. N2O emissions from activated sludge processes, 2008-2009: Results of a national surveying program in the United States. Environ. Sci. Technol., 44(12):4505-4511.

Andrianisa, H.,A., Ito, A., Sasaki, A., Aizawa, J., and Umita, T. 2008. Biotransformation of arsenic species by activated sludge and removal of bio-oxidised arsenate from wastewater by coagulation with ferric chloride. Water Research, 42(19), pp. 4809-4817

Andrianisa, H.,A., Ito, A., Sasaki, A., Ikeda, M., Aizawa, J., and Umita, T. 2006. Behaviour of arsenic species in batch activated sludge process: biotransformation and removal. Water Science and Technology, 54(8), pp. 121-128.

Burbano, A and Brandhuber, P. (2012) Demonstration of membrane zero liquid discharge for drinking water systems. Water Environment Research Federation (WERF) Report WERF5T10.

California Air Resources Board, ICLEI, California Climate Action Registry, The Climate Registry. 2008. Local Government Operations Protocol. For the quantification and reporting of greenhouse gas emissions inventories, Version 1.1.

Chung, B., Cho, J., Song, C., and Park, B. Degradation of naturally contaminated polycyclic aromatic hydrocarbons in municipal sewage sludge by electron beam irradiation. Bulletin of Environmental Contamination and Toxicology, 81(1), pp. 7-11.

CRITFC (Columbia River Inter-Tribal Fish Commission). 1994. A fish consumption survey of the Umatilla, Nez Perce, Yakama and Warm Springs Tribes of the Columbia River Basin. Columbia River Inter-Tribal Fish Commission Report reference #94-03, Portland, Oregon.

Eckenfelder, W.W., Industrial Water Pollution Control, 2nd ed. (New York: McGraw-Hill, 1989).

Ecology. 2010. (Lubliner, B., M. Redding, and D. Ragsdale). Pharmaceuticals and Personal Care Products in Municipal Wastewater and Their Removal by Nutrient Treatment Technologies. Washington State Department of Ecology, Olympia, WA. Publication Number 10-03-004.

González, D., Ruiz, L.M., Garralón, G., Plaza, F., Arévalo, J., Parada, J., Péreza, J., Morenoa, B., and Ángel Gómez, M. 2012. Wastewater polycyclic aromatic hydrocarbons removal by membrane bioreactor. Desalination and Water Treatment, 42, pp. 94–99

Grosser, J. 2010. The Challenge: Measure Arsenic in Drinking Water. White paper.

Haapeaa, P., and Tuhkanen, T. 2006. Integrated treatment of PAH contaminated soil by soil washing, ozonation and biological treatment . Journal of Hazardous Materials,136(21), pp. 244–250

Intergovernmental Panel on Climate Change. 2006. 2006 IPCC Guidelines for National Greenhouse Gas Inventories. Prepared by the National Greenhouse Gas Inventories Programme, Eggleston, S., Buendia, L., Miwa, K., Ngara, T., Tanabe, K. (eds.) Published: IGES, Japan.

LaGrega, M.D., Buckingham P.L. and Evans J.C., Hazardous Waste Management, 1st ed. (New York: McGraw-Hill, 1994).

Melcer, H., Steel, P., and Bedford, W.K. 1993. Removal of polycyclic aromatic hydrocarbons and hetercyclic nitrogenous compounds by a POTW receiving industrial discharges. Proceeding of WEFTEC 1993.

Mickley and Associates. 2006. Membrane Concentrate Disposal: Practices and Regulations. U.S. Department of the Interior, Bureau of Reclamation, Contract No. 98-FC-81-0054.

National Council for Air and Stream Improvement, Inc. (NCASI). 1998. Technical and economic feasibility assessment of metals reduction in pulp and paper mill wastewaters. Technical Bulletin No. 756. Research Triangle Park, NC: National Council for Air and Stream Improvement, Inc., 1998.

National Council for Air and Stream Improvement, Inc. (NCASI). 2004. Investigation of advanced techniques to remove low-level mercury from pulp and paper mill effluents. Technical Bulletin No. 870. Research Triangle Park, NC: National Council for Air and Stream Improvement, Inc.

National Council for Air and Stream Improvement, Inc. (NCASI). 2000. Memorandum: Information on PCB Water Quality Criteria, Analytical Methods, and Measurement Results for Point Sources and Ambient Waters. Technical Bulletin No. 807. Research Triangle Park, NC: National Council for Air and Stream Improvement, Inc.

National Council for Air and Stream Improvement, Inc. (NCASI). 2000. Bench scale testing of processes to reduce metals concentrations in pulp and paper mill wastewaters. Technical Bulletin No. 807. Research Triangle Park, NC: National Council for Air and Stream Improvement, Inc.

Ning, R. 2002. Arsenic removal by reverse osmosis. Desalination, 143 (3), pp. 237–241

Oleszczuk, P., Hale, S. E., Lehmann, J., and Cornelissen, G. 2012. Activated carbon and biochar amendments decrease pore-water concentrations of polycyclic aromatic hydrocarbons (PAHs) in sewage sludge. Bioresource Technology, 111, pp. 84–91

Oregon Department of Environmental Quality. 2011. Table 40: Human Health Water Quality Criteria for Toxic Pollutants, Effective October 17, 2011. Available on-line at: http://www.deq.state.or.us/wq/standards/toxics.htm

Owen, W.F. 1982. Energy in Wastewater Treatment. Prentice-Hall, Englewood Cliffs, New Jersey.

Parker, W., Monteith, H., and Pileggi, V. 2009. Estimation of Biodegradation and Liquid-Solid Partitioning Coefficients for Complex PAHs in Wastewater Treatment. Proceedings of the Water Environment Federation 2009, pp. 2537-2554.

Rodrigue, P., and Rielly, A. 2009. Effectiveness of a membrane bioreactor on weak domestic wastewater containing polychlorinated biphenyls. Proceedings of the Water Environment Federation, Microconstituents and Industrial Water Quality 2009, pp. 174-184(11)

Russo, L., Rizzo, L., and Belgiorno, V. 2012. Ozone oxidation and aerobic biodegradation with spent mushroom compost for detoxification and benzo(a)pyrene removal from contaminated soil. Chemosphere, 87(6), pp. 595-601

SimaPro 6. 2008. Life Cycle Analysis Software. The Netherlands.

Sponza, D., and Oztekin, R. 2010. Effect of sonication assisted by titanium dioxide and ferrous ions on polyaromatic hydrocarbons (PAHs) and toxicity removals from a petrochemical industry wastewater in Turkey. Journal of Chemical Technology & Biotechnology, 85(7), pp. 913-925

U.S. Environmental Protection Agency (EPA). 2003. Arsenic Treatment Technology Handbook for Small Systems, EPA 816R03014.

U.S. Environmental Protection Agency. 2000. Methodology for Deriving Ambient Water Quality Criteria for the Protection of Human Health. EPA- 822-B-00-004, October 2000.

U.S. Environmental Protection Agency. 2007. The Emissions & Generation Resource Integrated Database – eGrid WebVersion1.0. United States Environmental Protection Agency, Washington, D.C.

U.S. Department of Agriculture (USDA). 1998. Continuing survey of food intakes by individuals: 1994-96, 1998. U.S. Department of Agriculture, Agricultural Research Service.

Water Environment Federation. 2009. Design of Municipal Wastewater Treatment Plants, WEF Manual of Practice 8, Fourth Edition, ASCE Manuals and Reports on Engineering Practice No. 76, Volume 1. Alexandria, VA.

Water Environment Research Foundation (WERF). 2012. Demonstration of Membrane Zero Liquid Discharge for Drinking Water Systems, A Literature Review. WERF5T10.

Water Environment Research Foundation (WERF). 2011. Striking the Balance Between Nutrient Removal in Wastewater Treatment and Sustainability. NUTR1R06n.

WesTech brochure. Victorville case study. Vendor Brochure.

Williams, M. 2003. A Review of Wastewater Treatment by Reverse Osmosis. White paper

Yerushalmi, L., Nefil, S., Hausler, R., and Guiot, S. 2006. Removal of pyrene and benzo(a)pyrene from contaminated water by sequential and simultaneous ozonation and biotreatment. Water Environment Research, 78 (11).

Zeng, Y., Hong, A., and Wavrek, D. 2000. Integrated chemical-biological treatment of benzo[a]pyrene. Environmental Science and Technology, 34 (5), pp 854–862

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7.0 Appendices

- Appendix A - Unit Process Sizing Criteria
- Appendix B - Greenhouse Gas Emissions Calculation Assumptions

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APPENDIX A - UNIT PROCESS SIZING CRITERIA

Table A-1. Unit Processes Sizing Criteria for Each Alternative

Unit Process	Units	Baseline Treatment	Advanced Treatment	Comment
Influent Pumping Station	unitless	3 Times Ave Flow	3 Times Ave Flow	This is peaking factor used to size the pumps (peak flow:average flow)
Alum Dose for CEPT (optional)	mg/L	20	20	This is the metal salt upstream of the primaries
Primary Clarifiers	gpd/sf	1000	1000	This is for average annual flows
Primary Solids Pumping Station	unitless	1.25 Times Ave Flow	1.25 Times Ave Flow	This is peaking factor used to size the pumps (maximum month flow:average flow)
Aeration System Oxygen Uptake Rate (OUR)	mg/L/hr	25	25	Average annual OUR is used in tandem with mixed liquor to determine the required aeration basin volume (the limiting parameter governs the activated sludge basin volume)
Aeration Basin Mixed Liquor	mg/L	1250	2500	Average annual mixed liquor is used in tandem with OUR (see next row) to determine the required aeration basin volume (the limiting parameter governs the activated sludge basin volume)
Secondary Clarifiers Hydraulic Loading	gpd/sf	650	--	Only use for Baseline as clarifiers governed hydraulically with short SRT (<2 days)
Secondary Clarifiers Solids Loading	lb/d/sf	--	24	Only use for Advanced Treatment as clarifiers governed by solids with long SRT (>8 days)
Return Activated Sludge (RAS) Pumping Station	unitless	1.25 Times Ave Flow	1.25 Times Ave Flow	RAS must have capacity to meet 100% influent max month Flow. The influent flow is multiplied by this peaking factor to determine RAS pumping station capacity.
Waste Activated Sludge (WAS) Pumping Station	gpm	1.25 Times Ave Flow	1.25 Times Ave Flow	WAS must have capacity to meet max month WAS flows. The average annual WAS flow is multiplied by this peaking factor to determine WAS pumping station capacity.
Microfiltration (MF) Flux	gfd	--	25	Based on average annual pilot experience in Coeur D'Alene, ID
MF Backwash Storage Tank	unitless	--	1.25	Storage tanks must have capacity to meet maximum month MF backwash flows. The average annual MF backwash volume is multiplied by this peaking factor to determine required volume.

Table A-1. Unit Processes Sizing Criteria for Each Alternative

Unit Process	Units	Baseline Treatment	Advanced Treatment	Comment
MF Backwash Pumps	unitless	--	1.25	Backwash pumps must have capacity to meet maximum month MF backwash flows. The average annual MF backwash flow is multiplied by this peaking factor to determine required flows.
Reverse Osmosis (RO)	gallon per square foot per day (gfd)	--	10	
RO Reject	%	--	20	This represents the percentage of feed flow that is rejected as brine
Chlorination Dose	mg/L	15	15	
Chlorination Storage Capacity	days	14	14	
Chlorine Contact Tank	min	30	30	This is for average annual conditions.
Dechlorination Dose	mg/L	15	15	
Dechlorination Storage Capacity	days	14	14	
Gravity Belt Thickener	gpm/m	200	200	This is for maximum month conditions using the 1.25 peaking factor from average annual to maximum month
Anaerobic Digestion	Hydraulic residence time (HRT)	18	18	This is for average annual conditions
Dewatering Centrifuge	gpm	120	120	This is for maximum month conditions using the 1.25 peaking factor from average annual to maximum month

gpd=gallons per day; sf=square feet; gpm=gallons per minute

Appendix B – Greenhouse Gas Emissions Calculation Assumptions

The steady state mass balance results were used to calculate GHG emissions. The assumptions used to convert between energy demand, chemical demand and production, as well as biologically-mediated gases (i.e., CH4 and N2O) and GHG emissions are provided in Table B-1. The assumptions are based on EPA (2007) values for energy production, an adaptation of the database provided in Ahn et al. (2010) for N2O emissions contribution, Intergovernmental Panel on Climate Change (IPCC) (2006) for fugitive CH4 emissions, and various resources for chemical production and hauling from production to the wastewater treatment plant (WWTP). Additionally, the biogas produced during anaerobic digestion that is used as a fuel source is converted to energy with MOP8 (2009) recommended waste-to-energy values.

Table B-1. Greenhouse Gas Emissions Assumptions

Parameters	Units	Value	Source
N_2O to CO_2 Conversion	lb CO_2/lb N_2O	296	IPCC, 2006
CH_4 to CO_2 Conversion	lb CO_2/lb CH_4	23	IPCC, 2006
Energy Production			
CO_2	lb CO_2/MWh	1,329	USEPA (2007)
N_2O	lb N_2O/GWh	20.6	USEPA (2007)
CH_4	lb CO_2/GWh	27.3	USEPA (2007)
Sum Energy Production	lb CO_2/MWh	1336	USEPA (2007)
GHGs per BTU Natural Gas			
CO_2	lb CO_2/MMBTU Natural Gas	52.9	CA Climate Action Registry Reporting Tool
N_2O	lb N_2O/MMBTU Natural Gas	0.0001	CA Climate Action Registry Reporting Tool
CH_4	lb CO_2/MMBTU Natural Gas	0.0059	CA Climate Action Registry Reporting Tool
Sum Natural Gas		53.1	CA Climate Action Registry Reporting Tool
Non-BNR N_2O Emissions	g N_2O/PE/yr	32	Ahn et al. (2010)
BNR N_2O Emissions	g N_2O/PE/yr	30	Ahn et al. (2010)
Biogas Purity	% Methane	65	WEF, 2009
Biogas to Energy	BTU/cf CH4	550	WEF, 2009
Digester Gas to Electrical Energy Transfer Efficiency	%	32	HDR Data

Table B-1. Greenhouse Gas Emissions Assumptions

Parameters	Units	Value	Source
Chemical Production			
Alum	lb CO_2/lb Alum	0.28	SimaPro 6.0 - BUWAL250, Eco-indicator 95
Polymer	lb CO_2/lb Polymer	1.18	Owen (1982)
Sodium Hypochlorite	lb CO_2/lb Sodium Hypochlorite	1.07	Owen (1982)
Building Energy Efficiency	kBTU/sf/yr	60	Calif. Commercial End-Use Survey (2006)
Hauling Distance		-	
Local	miles	100	-
Hauling Emissions			
Fuel Efficiency	miles per gallon	8	
CO_2	kg CO_2/gal diesel	10.2	CA Climate Action Registry Reporting Tool
N_2O	kg N_2O/gal diesel	0.0001	CA Climate Action Registry Reporting Tool
CH_4	kg CH_4/gal diesel	0.003	CA Climate Action Registry Reporting Tool
Sum Hauling Fuel	kg CO_2/gal diesel	10.2	CA Climate Action Registry Reporting Tool

GWh = Giga Watt Hours
MWh = Mega Watt Hours
MMBTU = Million British Thermal Units
BTU = British Thermal Unit
PE = Population Equivalents
kBTU/sf/yr = 1,000 British Thermal Units per Square Foot per Year
cf = cubic feet
lb = pound
kg = kilogram
gal = gallon

Comparison of EPA's 2015 Final Updated Human Health AWQC and Previous AWQC
June 2015

Pollutant	CAS No.	2015 EPA Human Health AWQC for the Consumption of		Previous EPA Human Health AWQC for the Consumption of	
		Water + Organism (µg/L)	Organism Only (µg/L)	Water + Organism (µg/L)	Organism Only (µg/L)
1,1,1-Trichloroethane	71-55-6	10,000	200,000	*	---
1,1,2,2-Tetrachloroethane	79-34-5	0.2	3	0.17	4
1,1,2-Trichloroethane	79-00-5	0.55	8.9	0.59	16
1,1-Dichloroethylene	75-35-4	300	20,000	330	7,100
1,2,4,5-Tetrachlorobenzene	95-94-3	0.03	0.03	0.97	1.1
1,2,4-Trichlorobenzene	120-82-1	0.071	0.076	35	70
1,2-Dichlorobenzene	95-50-1	1,000	3,000	420	1,300
1,2-Dichloroethane	107-06-2	9.9	650	0.38	37
1,2-Dichloropropane	78-87-5	0.90	31	0.5	15
1,2-Diphenylhydrazine	122-66-7	0.03	0.2	0.036	0.2
1,3-Dichlorobenzene	541-73-1	7	10	320	960
1,3-Dichloropropene	542-75-6	0.27	12	0.34	21
1,4-Dichlorobenzene	106-46-7	300	900	63	190
2,4,5-Trichlorophenol	95-95-4	300	600	1,800	3,600
2,4,6-Trichlorophenol	88-06-2	1.5	2.8	1.4	2.4
2,4-Dichlorophenol	120-83-2	10	60	77	290
2,4-Dimethylphenol	105-67-9	100	3,000	380	850
2,4-Dinitrophenol	51-28-5	10	300	69	5,300
2,4-Dinitrotoluene	121-14-2	0.049	1.7	0.11	3.4
2-Chloronaphthalene	91-58-7	800	1,000	1,000	1,600
2-Chlorophenol	95-57-8	30	800	81	150
2-Methyl-4,6-Dinitrophenol	534-52-1	2	30	13	280
3,3'-Dichlorobenzidine	91-94-1	0.049	0.15	0.021	0.028
3-Methyl-4-Chlorophenol	59-50-7	500	2,000	*	*
Acenaphthene	83-32-9	70	90	670	990
Acrolein	107-02-8	3	400	6	9

Comparison of EPA's 2015 Final Updated Human Health AWQC and Previous AWQC
June 2015

Pollutant	CAS No.	2015 EPA Human Health AWQC for the Consumption of		Previous EPA Human Health AWQC for the Consumption of	
		Water + Organism (µg/L)	Organism Only (µg/L)	Water + Organism (µg/L)	Organism Only (µg/L)
Acrylonitrile	107-13-1	0.061	7.0	0.051	0.25
Aldrin	309-00-2	0.00000077	0.00000077	0.000049	0.00005
alpha-Hexachlorocyclohexane (HCH)	319-84-6	0.00036	0.00039	0.0026	0.0049
alpha-Endosulfan	959-98-8	20	30	62	89
Anthracene	120-12-7	300	400	8,300	40,000
Benzene	71-43-2	0.58 - 2.1	16 - 58	0.61 - 2.2	14 - 51
Benzidine	92-87-5	0.00014	0.011	0.000086	0.0002
Benzo(a)anthracene	56-55-3	0.0012	0.0013	0.0038	0.018
Benzo(a)pyrene	50-32-8	0.00012	0.00013	0.0038	0.018
Benzo(b)fluoranthene	205-99-2	0.0012	0.0013	0.0038	0.018
Benzo(k)fluoranthene	207-08-9	0.012	0.013	0.0038	0.018
beta-Hexachlorocyclohexane (HCH)	319-85-7	0.0080	0.014	0.0091	0.017
beta-Endosulfan	33213-65-9	20	40	62	89
Bis(2-Chloro-1-Methylethyl) Ether	108-60-1	200	4,000	1,400	65,000
Bis(2-Chloroethyl) Ether	111-44-4	0.030	2.2	0.03	0.53
Bis(2-Ethylhexyl) Phthalate	117-81-7	0.32	0.37	1.2	2.2
Bis(Chloromethyl) Ether	542-88-1	0.00015	0.017	0.0001	0.00029
Bromoform	75-25-2	7.0	120	4.3	140
Butylbenzyl Phthalate	85-68-7	0.10	0.10	1,500	1,900
Carbon Tetrachloride	56-23-5	0.4	5	0.223	1.6
Chlordane	57-74-9	0.00031	0.00032	0.0008	0.00081
Chlorobenzene	108-90-7	100	800	130	1,600
Chlorodibromomethane	124-48-1	0.80	21	0.4	13
Chloroform	67-66-3	60	2,000	5.7	470
Chlorophenoxy Herbicide (2,4-D)	94-75-7	1,300	12,000	100	---
Chlorophenoxy Herbicide (2,4,5-TP) [Silvex]	93-72-1	100	400	10	---

Comparison of EPA's 2015 Final Updated Human Health AWQC and Previous AWQC
June 2015

Pollutant	CAS No.	2015 EPA Human Health AWQC for the Consumption of		Previous EPA Human Health AWQC for the Consumption of	
		Water + Organism (µg/L)	Organism Only (µg/L)	Water + Organism (µg/L)	Organism Only (µg/L)
Chrysene	218-01-9	0.12	0.13	0.0038	0.018
Cyanide	57-12-5	4	400	140	140
Dibenzo(a,h)anthracene	53-70-3	0.00012	0.00013	0.0038	0.018
Dichlorobromomethane	75-27-4	0.95	27	0.55	17
Dieldrin	60-57-1	0.0000012	0.0000012	0.000052	0.000054
Diethyl Phthalate	84-66-2	600	600	17,000	44,000
Dimethyl Phthalate	131-11-3	2,000	2,000	270,000	1,100,000
Di-n-Butyl Phthalate	84-74-2	20	30	2,000	4,500
Dinitrophenols	25550-58-7	10	1,000	69	5,300
Endosulfan Sulfate	1031-07-8	20	40	62	89
Endrin	72-20-8	0.03	0.03	0.059	0.06
Endrin Aldehyde	7421-93-4	1	1	0.29	0.3
Ethylbenzene	100-41-4	68	130	530	2,100
Fluoranthene	206-44-0	20	20	130	140
Fluorene	86-73-7	50	70	1,100	5,300
gamma-Hexachlorocyclohexane (HCH)	58-89-9	4.2	4.4	0.98	1.8
Heptachlor	76-44-8	0.0000059	0.0000059	0.000079	0.000079
Heptachlor Epoxide	1024-57-3	0.000032	0.000032	0.000039	0.000039
Hexachlorobenzene	118-74-1	0.000079	0.000079	0.00028	0.00029
Hexachlorobutadiene	87-68-3	0.01	0.01	0.44	18
Hexachlorocyclohexane (HCH)-Technical	608-73-1	0.0066	0.010	0.0123	0.0414
Hexachlorocyclopentadiene	77-47-4	4	4	40	1,100
Hexachloroethane	67-72-1	0.1	0.1	1.4	3.3
Indeno(1,2,3-cd)pyrene	193-39-5	0.0012	0.0013	0.0038	0.018
Isophorone	78-59-1	34	1,800	35	960
Methoxychlor	72-43-5	0.02	0.02	100	---

Comparison of EPA's 2015 Final Updated Human Health AWQC and Previous AWQC
June 2015

Pollutant	CAS No.	2015 EPA Human Health AWQC for the Consumption of		Previous EPA Human Health AWQC for the Consumption of	
		Water + Organism (µg/L)	Organism Only (µg/L)	Water + Organism (µg/L)	Organism Only (µg/L)
Methyl Bromide	74-83-9	100	10,000	47	1,500
Methylene Chloride	75-09-2	20	1,000	4.6	590
Nitrobenzene	98-95-3	10	600	17	690
Pentachlorobenzene	608-93-5	0.1	0.1	1.4	1.5
Pentachlorophenol	87-86-5	0.03	0.04	0.27	3
Phenol	108-95-2	4,000	300,000	10,000	860,000
p,p'-Dichlorodiphenyldichloroethane (DDD)	72-54-8	0.00012	0.00012	0.00031	0.00031
p,p'-Dichlorodiphenyldichloroethylene (DDE)	72-55-9	0.000018	0.000018	0.00022	0.00022
p,p'-Dichlorodiphenyltrichloroethane (DDT)	50-29-3	0.000030	0.000030	0.00022	0.00022
Pyrene	129-00-0	20	30	830	4,000
Tetrachloroethylene (Perchloroethylene)	127-18-4	10	29	0.69	3.3
Toluene	108-88-3	57	520	1,300	15,000
Toxaphene	8001-35-2	0.00070	0.00071	0.00028	0.00028
trans-1,2-Dichloroethylene (DCE)	156-60-5	100	4,000	140	10,000
Trichloroethylene (TCE)	79-01-6	0.6	7	2.5	30
Vinyl Chloride	75-01-4	0.022	1.6	0.025	2.4

*AWQC for this chemical were not provided in EPA's previous update.

United States Environmental Protection Agency

Office of Water
EPA 820-F-15-001
June 2015

Human Health Ambient Water Quality Criteria: 2015 Update

Summary

EPA published final updated ambient water quality criteria for the protection of human health for 94 chemical pollutants. These updated recommendations reflect the latest scientific information and EPA policies, including updated body weight, drinking water consumption rate, fish consumption rate, bioaccumulation factors, health toxicity values, and relative source contributions. EPA accepted written scientific views from the public from May to August 2014 on the draft updated human health criteria and has published responses to those comments. EPA water quality criteria serve as recommendations to states and tribes authorized to establish water quality standards under the Clean Water Act.

Background

Ambient water quality criteria developed by EPA under Clean Water Act section 304(a) represent specific levels of chemicals or conditions in a water body that are not expected to cause adverse effects to human health. EPA is required to develop and publish water quality criteria that reflect the latest scientific knowledge. These criteria are not rules, nor do they automatically become part of a state's water quality standards. States may adopt the criteria that EPA publishes, modify EPA's criteria to reflect site-specific conditions, or adopt different criteria based on other scientifically-defensible methods. EPA must, however, approve any new water quality standards adopted by a state before they can be used for Clean Water Act purposes.

In this 2015 update, EPA revised 94 of the existing human health criteria to reflect the latest scientific information, including updated exposure factors (body weight, drinking water consumption rates, fish consumption rate), bioaccumulation factors, and toxicity factors (reference dose, cancer slope factor). The criteria have also been updated to follow the current EPA methodology for deriving human health criteria (USEPA 2000). EPA also developed chemical-specific science documents for each of the 94 chemical pollutants. The science documents detail the latest scientific information supporting the updated final human health criteria, particularly the updated toxicity and exposure input values. Specific updates are described below.

Due to outstanding technical issues, EPA did not update human health criteria for the following chemical pollutants at this time: antimony, arsenic, asbestos, barium, beryllium, cadmium, chromium (III or VI), copper, manganese, methylmercury, nickel, nitrates, nitrosamines, N-nitrosodibutylamine, N-nitrosodiethylamine, N-nitrosopyrrolidine, N-nitrosodimethylamine, N-nitrosodi-n-propylamine, N-nitrosodiphenylamine, polychlorinated biphenyls (PCBs), selenium, thallium, zinc, or 2,3,7,8-TCDD (dioxin).

It is important for states and authorized tribes to consider any new or updated section 304(a) criteria as part of their triennial review to ensure that state or tribal water quality standards reflect current science and protect applicable designated uses. EPA recently proposed revisions to its water quality

standards regulations that would, if finalized without substantive change, require states during their triennial reviews to consider new or updated section 304(a) recommended criteria and, if they do not adopt new or revised criteria for such pollutants, provide an explanation to EPA as to why the state did not do so. These final updated human health criteria recommendations supersede EPA's previous recommendations.

Updated Exposure Inputs

Body Weight

EPA updated the default body weight for human health criteria to 80 kilograms based on National Health and Nutrition Examination Survey (NHANES) data from 1999 to 2006 (USEPA 2011). This represents the mean body weight for adults ages 21 and older. EPA's previously recommended default body weight was 70 kilograms, which was based on the mean body weight of adults from the NHANES III database (1988-1994).

Drinking Water

EPA updated the default drinking water consumption rate to 2.4 liters per day based on NHANES data from 2003 to 2006 (USEPA 2011). This represents the per capita estimate of community water ingestion at the 90th percentile for adults ages 21 and older. EPA previously recommended a default drinking water consumption rate of 2 liters per day, which represented the per capita community water ingestion rate at the 86th percentile for adults surveyed in the US Department of Agriculture's 1994-1996 Continuing Survey of Food Intake by Individuals (CSFII) analysis and the 88th percentile of adults in the National Cancer Institute study of the 1977-1978 Nationwide Food Consumption Survey.

Fish Consumption

EPA updated the default fish consumption rate to 22 grams per day. This rate represents the 90th percentile consumption rate of fish and shellfish from inland and nearshore waters for the U.S. adult population 21 years of age and older, based on NHANES data from 2003 to 2010 (USEPA 2014). EPA's previously recommended rate of 17.5 grams per day was based on the 90th percentile consumption rate of fish and shellfish from inland and nearshore waters for the U.S. adult population and was derived from 1994-1996 CSFII data.

As described in EPA's human health criteria methodology (USEPA 2000), the level of fish consumption in highly exposed populations varies by geographical location. Therefore, EPA suggests a four preference hierarchy for states and authorized tribes that encourages use of the best local, state, or regional data available to derive fish consumption rates. EPA recommends that states and authorized tribes consider developing criteria to protect highly exposed population groups and use local or regional data in place of a default value as more representative of their target population group(s). The preferred hierarchy is: (1) use of local data; (2) use of data reflecting similar geography/ population groups; (3) use of data from national surveys; and (4) use of EPA's default consumption rates.

Bioaccumulation Factors

EPA's methodology for deriving human health criteria emphasizes using, when possible, measured or estimated bioaccumulation factors (BAFs), which account for chemical accumulation in aquatic organisms from all potential exposure routes (USEPA 2000). Unlike bioconcentration factors, BAFs account for more exposure pathways than direct water contact. As a result, the updated criteria will better represent exposures to pollutants that affect human health. In order to account for the variation in bioaccumulation that is due to trophic position of the organism, EPA's methodology (USEPA 2000) recommends that BAFs be determined and applied to three trophic levels of fish.

EPA selected BAFs using a framework for deriving national trophic level-specific BAFs (USEPA 2000; USEPA 2003). EPA used field-measured BAFs and laboratory-measured bioconcentration factors available from peer-reviewed, publicly available databases to develop national BAFs. If this information was not available, EPA selected octanol-water partition coefficients (Kow values) from peer-reviewed sources for use in calculating national BAFs. As an additional line of evidence, EPA reported model-estimated BAFs for every chemical based on

the Estimation Program Interface (EPI) Suite (USEPA 2012) to support the field-measured or predicted BAFs.

Updated Health Toxicity Values

EPA considered all available toxicity values for both noncarcinogenic and carcinogenic toxicological effects to develop the updated human health criteria. EPA's Integrated Risk Information System (IRIS) was the primary source for reference dose and cancer slope factors for this update. For some pollutants, however, more recent toxicity assessments were provided by EPA's Office of Water, EPA's Office of Pesticide Programs, and international or state agencies. EPA followed a systematic process to search for and select the toxicity values used to derive the final updated human health criteria for noncarcinogenic and carcinogenic effects.

Relative Source Contribution

EPA updated the human health criteria to reflect chemical-specific relative source contributions (RSC) ranging from 20 to 80 percent following the Exposure Decision Tree approach described in EPA's methodology (USEPA 2000). EPA recommends inclusion of an RSC when developing human health criteria for threshold non-carcinogens or non-linear carcinogens. The RSC allows a percentage of the reference dose's exposure to be attributed to ambient water and fish consumption (including fish and shellfish from inland and nearshore waters) when there are other potential exposure sources. The rationale for this approach is that the objective of the water quality criteria is to ensure that an individual's total exposure from all sources does not exceed the criteria. Exposures outside of the RSC include, but are not limited to, exposure to a particular pollutant from ocean fish consumption (not included in the fish consumption rate), non-fish food consumption (meats, poultry, fruits, vegetables, and grains), dermal exposure, and respiratory exposure.

Where can I find more information?

To access the Federal Register notice, the final updated criteria, and supporting documents visit EPA's National Recommended Human Health Criteria website at: http://water.epa.gov/scitech/swguidance/standards/criteria/health/.

References

USEPA. 2000. *Methodology for Deriving Ambient Water Quality Criteria for the Protection of Human Health (2000)*. EPA-822-B-00-004. U.S. Environmental Protection Agency, Office of Water, Office of Science and Technology, Washington, DC. Accessed February 2015. http://water.epa.gov/scitech/swguidance/standards/upload/2005_05_06_criteria_humanhealth_method_complete.pdf.

USEPA. 2003. *Methodology for Deriving Ambient Water Quality Criteria for the Protection of Human Health (2000), Technical Support Document. Vol. 2, Development of National Bioaccumulation Factors*. EPA-822-R-03-030. U.S. Environmental Protection Agency, Office of Water, Office of Science and Technology, Washington, DC. Accessed March 2015. http://www.epa.gov/scipoly/sap/meetings/2008/october/methodology.pdf.

USEPA. 2011. *Exposure Factors Handbook: 2011 Edition*. EPA-600-R-09-052F. U.S. Environmental Protection Agency, Office of Research and Development, Washington, DC. Accessed February 2015. http://www.epa.gov/ncea/efh/pdfs/efh-complete.pdf.

USEPA. 2012. *Estimation Programs Interface (EPI) Suite™ for Microsoft® Windows, v 4.10*. U.S. Environmental Protection Agency, Office of Pollution Prevention and Toxics, Washington, DC. Accessed February 2015. http://www.epa.gov/oppt/exposure/pubs/episuite.htm.

USEPA. 2014. *Estimated Fish Consumption Rates for the U.S. Population and Selected Subpopulations (NHANES 2003-2010)*. EPA-820-R-14-002. U.S. Environmental Protection Agency, Office of Water, Washington, DC. Accessed February 2015. http://water.epa.gov/scitech/swguidance/fishshellfish/fishadvisories/upload/Estimated-Fish-Consumption-Rates-for-the-U-S-Population-and-Selected-Subpopulations-NHANES-2003-2010.pdf.

Guidance for Implementing the January 2001 Methylmercury Water Quality Criterion

EPA 823-R-10-001 • April 2010

Guidance for Implementing the January 2001 Methylmercury Water Quality Criterion

Final

United States Environmental Protection Agency

Office of Science and Technology (4305T)
1200 Pennsylvania Ave., NW
Washington, DC 20460
EPA-823-R-10-001
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April 2010

DISCLAIMER

This guidance provides advice on how to implement the water quality criterion recommendation for methylmercury that the U.S. Environmental Protection Agency (EPA) published in January 2001. This guidance does not impose legally binding requirements on EPA, states, tribes, other regulatory authorities, or the regulated community, and may not apply to a particular situation based upon the circumstances. EPA, state, tribal, and other decision makers retain the discretion to adopt approaches on a case-by-case basis that differ from those in the guidance where appropriate. EPA may update this guidance in the future as better information becomes available.

The Office of Science and Technology, Office of Water, U.S. Environmental Protection Agency has approved this guidance for publication. Mention of trade names, products, or services does not convey and should not be interpreted as conveying official EPA approval, endorsement, or recommendation for use.

The suggested citation for this document is:

> USEPA. 2010. *Guidance for Implementing the January 2001 Methylmercury Water Quality Criterion*. EPA 823-R-10-001. U.S. Environmental Protection Agency, Office of Water, Washington, DC.

FOREWORD

On January 8, 2001, the U.S. Environmental Protection Agency (EPA) announced the availability of its recommended Clean Water Act (CWA) section 304(a) water quality criterion for methylmercury. This water quality criterion, 0.3 milligram (mg) methylmercury per kilogram (kg) fish tissue wet weight, describes the concentration of methylmercury in freshwater and estuarine fish and shellfish tissue that should not be exceeded to protect consumers of fish and shellfish among the general population. EPA recommends that states, territories, and authorized tribes use the criterion and this guidance in establishing or updating water quality standards for waters of the United States and in issuing fish and shellfish consumption advisories. States and authorized tribes remain free to adjust EPA's recommended criterion, provided that their new or revised water quality criteria protect the designated uses and are based on scientifically defensible methodology.

The publication of the 2001 methylmercury criterion was the first time EPA issued a water quality criterion expressed as a fish and shellfish tissue value rather than as a water column value. EPA recognizes that this approach differs from traditional water column criteria and might pose implementation challenges. In the January 8, 2001 Federal Register notice, EPA stated that it planned to develop more detailed guidance to help states, territories, and authorized tribes with implementation of the methylmercury criterion in water quality standards and related programs. This document provides that detailed guidance.

EPA wrote the *Guidance for Implementing the January 2001 Methylmercury Water Quality Criterion* to provide technical guidance to states, territories, and authorized tribes exercising responsibility under CWA section 303(c), which provides for state review and revision of water quality standards every three years, and adoption of criteria for toxic pollutants, such as mercury, for which EPA has published criteria under CWA section 304(a). The document provides guidance on how to use the new fish tissue-based criterion recommendation in developing water quality standards for methylmercury and in implementing those standards in Total Maximum Daily Loads (TMDLs) and National Pollutant Discharge Elimination System (NPDES) permits. EPA also wrote the guidance to discuss approaches for managing the development of TMDLs for waterbodies impaired by mercury and to recommend an approach for directly incorporating the methylmercury tissue criterion into NPDES permits.

For more information on the methylmercury criterion, see the criteria page on EPA's Web site at http://www.epa.gov/waterscience/criteria/methylmercury/index.html. For more information on EPA's water quality standards program, see the standards page on EPA's Web site at http://www.epa.gov/waterscience/standards. For more information about this guidance document, contact U.S. Environmental Protection Agency, Office of Science and Technology (4305T), 1200 Pennsylvania Avenue, NW, Washington, DC 20460.

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FIGURES

1 Executive Summary

In January 2001 EPA published ambient water quality criteria (AWQC) recommendations for methylmercury for the protection of people who eat fish and shellfish. This criterion, 0.3 milligram (mg) methylmercury per kilogram (kg) fish tissue wet weight, marks EPA's first issuance of a water quality criterion expressed as a fish and shellfish tissue value rather than as an ambient water column value.

Research shows that exposure to mercury and its compounds can cause certain toxic effects in humans and wildlife (USEPA 1997a). As of 2008, 50 states, 1 territory, and 3 tribes had issued fish consumption advisories for mercury covering 16.8 million lake acres and 1.3 million river miles (USEPA 2009a). Mercury is widely distributed in the environment and originates from natural and human-induced (anthropogenic) sources, including combustion and volcanoes. Methylmercury is highly bioaccumulative, especially in aquatic food webs. Nearly 100 percent of the mercury that bioaccumulates in upper-trophic-level fish (predator) tissue is methylmercury (Akagi et al. 1995; Becker and Bigham 1995; Bloom 1992; Kim 1995).

Under section 303(c) of the Clean Water Act (CWA), states and authorized tribes must adopt water quality criteria that protect designated uses. Section 303(c)(1) provides that states and authorized tribes review their water quality standards every three years and modify and adopt water quality standards as appropriate. In light of the new science used to develop the 2001 methylmercury fish tissue criterion, EPA believes that states should consider reviewing and revising their mercury human health criteria during their next triennial review. This document provides technical guidance to states and authorized tribes that exercise responsibility under CWA section 303(c) on how to use the new fish tissue-based criterion recommendation as they develop water quality standards for methylmercury.

EPA expects that, as states adopt methylmercury water quality criteria and as monitoring of effluents, receiving waters, and fish tissue with the more sensitive methods recommended by EPA increases, the number of waterbodies that states report on CWA section 303(d) lists as impaired due to methylmercury contamination might increase. This guidance is designed to assist states and authorized tribes to address those impairments. Furthermore, this guidance addresses coordination across various media and program areas in implementing the criterion, which will be important because atmospheric deposition and multimedia cycling of mercury are significant in many waterbodies.

EPA recognizes the complexity and comprehensive nature of this guidance. As is always the case when EPA issues technical guidance, EPA will provide outreach and technical assistance to states and authorized tribes in implementing this guidance.

The following tables (tables 1a through 1d) provide a brief summary of the most important recommendations applicable to states and authorized tribes that are contained in the guidance.

NOTE: These tables are provided as a convenience to the reader, but are not comprehensive and are not a substitute for the full content of the guidance contained in the other chapters of this document.

Table 1a. Recommendations for water quality standards adoption

	Most applicable to criteria expressed as…	For a full discussion see section…
Recommended form of a methylmercury criterion EPA recommends that states and authorized tribes adopt a methylmercury criterion expressed as a fish tissue value. When adopting a fish tissue criterion, states and authorized tribes will need to decide whether to:		3.1.2 and 3.1.3
• Implement the fish tissue criterion without water column translation, or	FT (fish tissue value)	
• Translate the fish tissue criterion to a water column value using bioaccumulation factors (BAFs). Three approaches include: 1. Site-specific BAFs 2. Modeled BAFs 3. BAFs derived using the results of field studies that are not site-specific (in limited circumstances); or	WC (water column value)	
• Combination (fish tissue criterion for some or all waters, combined with water column criteria for some or all waters).	Both FT and WC	
• States and authorized tribes may consider retaining their existing water column criteria, on a temporary basis, particularly for waters where there is a relatively high direct water input of mercury.	FT alone	
Adoption considerations	FT or WC	
• When adopting a fish tissue criterion, EPA encourages states and authorized tribes to develop implementation procedures.		3.1.2.1
• This guidance does not supersede requirements in EPA's Great Lakes Initiative (GLI) regulation for waters in the Great Lakes system.		5.1
Criterion adjustments • Adjusting for local fish consumption rates. • Adjusting for other sources of mercury (marine fish).	FT or WC	3.2.1
Mixing zones		5.3
• Not relevant when applying a fish tissue criterion that has not been translated to a water column value.	FT alone	
• If the fish tissue criterion is converted to water column values, EPA advises caution in the use of any mixing zones for mercury. Restricting or eliminating mixing zones may be appropriate.	WC	
Variances • Guidance on when variances are appropriate. • Considerations before granting a variance.	WC	3.2.2

Table 1b. Recommendations for monitoring and assessment

	Most applicable to criteria expressed as…	For a full discussion see section…
Recommended analytical methods		4.1
• Methods 1631, revision E and 245.7 for mercury in water.	WC	
• Draft Appendix A of Method 1631 for mercury in fish tissue.	FT	
• Method 1630 for methylmercury in water.	WC	
• Method 1630 (with draft modifications) for methylmercury in fish tissue.	FT	
Other available methods are listed in appendix C of this guidance.	FT or WC	App. C
Field sampling recommendations	FT alone	4.2
• Select fish for monitoring that are commonly eaten in the study area.		
• Choose large fish because these are typically highest in methylmercury.		
• If local consumption data are not available, match assumed consumption pattern to sampled species, or sample trophic level 4 species.		
• Use composite samples of fish fillets.		
• EPA recommends biennial sampling if resources allow, otherwise waterbodies should be screened a minimum of every 5 years.		
Assessing non-attainment of fish tissue criterion	FT alone	4.3
• Use statistical tests if enough data, or consider sample-by-sample comparisons if very limited data.		

Table 1c. Recommendations for total maximum daily loads (TMDLs)

	Most applicable to criteria expressed as…	For a full discussion see section…
States' timing of TMDL development • States with comprehensive mercury reduction programs in place may defer TMDLs for waters impaired by mercury mainly from atmospheric sources. (Summarizing EPA's voluntary "5m" category for listing impaired waters.) • The greater the relative contribution to a waterbody from mercury sources other than air deposition, such as water point sources, the more appropriate it may be to use the TMDL process to characterize and address those sources sooner, rather than deferring TMDL development.	FT or WC	6.2 and 7.5.2.2
Approaches in approved mercury TMDLs Examples in guidance text and appendix D discuss: • Types of mercury sources; tools for assessing point sources, atmospheric deposition, past metals mining activity, sediments, and natural sources. • Example allocation scenarios involving waters where predominant sources are air deposition or mining. • Post-TMDL monitoring.	FT or WC	6.2
Geographic scale Describes scales that have been used for developing mercury TMDLs: • Waterbody-specific. • Watershed-level. • Statewide or regional.	FT or WC	6.2.1
Available models and example TMDL applications • Example models for different situations (steady state, dynamic, detail geometry, regression). • Factors leading to model selection (methylation, BAFs, sediments). • Use of linked models without having explicit water column criteria or translations. • Other analytical approaches, e.g., proportionality approach: Where air deposition is the only significant mercury source and steady-state conditions apply, TMDLs have been developed to meet fish tissue targets by relying on a proportional relationship between mercury deposition and fish tissue methylmercury concentration.	FT or WC FT alone FT	6.2.2.2 6.2.2.2.1

Table 1d. Recommendations for permitting procedures

	Most applicable to criteria expressed as…	For a full discussion see section…
Two implementation approaches		
• If a TMDL or a water column translation derived from a fish tissue criterion or site-specific data to translate is available at time of permit issuance, implement using the approaches described in the Technical Support Document (TSD) for Water Quality-based Controls (USEPA 1991).	WC	7.4
• If a TMDL or water column translation or site-specific data to translate are not available, implement approaches described below.	FT alone	7.5
Finding "reasonable potential" (RP)[a] Depending on the particular facts, a permitting authority may reasonably conclude that a facility has RP if: • There is a quantifiable level of mercury in the discharge, using a sufficiently sensitive EPA-approved analytical method and • Fish tissue from the receiving water is close to or exceeds the criterion.	FT alone	7.5.1
Where mercury effluent levels are unknown EPA recommends that permitting authorities: • Require effluent monitoring using a sufficiently sensitive EPA-approved analytical method. • Include a reopener clause in the permit to allow permit to be modified if effluent data indicate a water quality-based effluent limit (WQBEL) is necessary.	FT alone	7.5.1.1.1
Where quantifiable amounts of mercury are not found • If the permitting authority believes the monitoring data are representative of the discharge, no further permit conditions may be necessary.	FT alone	7.5.1.1.2
Where fish tissue concentrations are unknown EPA recommends that permitting authorities: • Include a special permit condition to conduct a mercury fish tissue survey for the receiving waterbody. • Include a reopener clause in the permit to allow permit to be modified if fish tissue data become available indicating a WQBEL is necessary. • Encourage the permittee to develop and implement a mercury minimization plan (MMP) tailored to the facility's potential to discharge mercury.	FT alone	7.5.1.2.1

Table 1d. Recommendations for permitting procedures *(continued)*

	Most applicable to criteria expressed as…	For a full discussion see section…
Permits with quantifiable mercury but without RP Where a discharge contains a quantifiable amount of mercury but fish tissue in the receiving water does not exceed the criterion: • If the discharger will undertake an activity that could result in an increase in receiving water or fish tissue mercury concentration o Conduct tier 2 antidegradation analysis and develop appropriate permit conditions. o Require permittee to implement an MMP tailored to the facility's potential to discharge mercury. o Require effluent monitoring. • If the discharger will not undertake an activity that could result in an increase in receiving water or fish tissue mercury concentration: o Encourage the facility to develop and implement an MMP tailored to the facility's potential to discharge mercury.	FT alone	7.5.1.2.2
Other factors in determining RP • EPA recommends that the permitting authority account for other factors that may constitute the basis for a finding of RP. These include rising fish tissue concentrations and the impact on downstream waters.	FT alone	7.5.1.2.2
Mercury in intake water • Where the only source of mercury in a discharge may be the intake water taken directly from the same body of water, and where there are no known sources or additional contributions of mercury at the facility, the permitting authority may reasonably conclude, based on the particular facts, that there is no RP to exceed water quality standards.	FT or WC	7.5.1.3

Table 1d. Recommendations for permitting procedures *(continued)*

	Most applicable to criteria expressed as…	For a full discussion see section…
WQBELs where there is a finding of RP[b] EPA recommends that permitting authorities: • Require the permittee to implement an MMP tailored to its potential to discharge mercury. • Depending on the particular facts, the permitting authority should consider including in an MMP an effluent trigger level, a mercury reduction goal, or an enforceable numeric level representing existing effluent quality or some increment of the mercury reduction determined achievable as a result of the measures and practices specified in the MMP. • Require effluent monitoring using a sufficiently sensitive EPA-approved method to enable evaluation of the effectiveness and implementation of the MMP. • Include a reopener clause to modify the permit conditions if the MMP is found to be not effective or if a water column translation of the criterion is developed. Other considerations and requirements may be necessary: • Where a discharger undertakes an activity that could result in an increase in receiving water or fish tissue mercury concentrations, it must be consistent with applicable antidegradation requirements. Additional requirements may also be necessary under the CWA and EPA's NPDES regulations. • Include appropriate technology-based limits pursuant to CWA section 301(b) and 40 CFR sections 125.3 and 122.44(a)(1). • For modified or reissued permits with existing effluent limits for mercury, any less stringent effluent limit must be consistent with anti-backsliding requirements.	FT alone	7.5.2.1 7.2.4

Table 1d. Recommendations for permitting procedures *(continued)*

	Most applicable to criteria expressed as…	For a full discussion see section…
Permits with RP where direct water inputs are relatively high In addition to the above: • EPA recommends that states and authorized tribes specifically consider developing TMDLs in the short term. • Where a state or tribe chooses not to develop a TMDL in the short term, the state or tribe should develop an analysis of sources and loading capacity similar to what a TMDL would provide, or a water column translation of the fish tissue criterion. • EPA recommends that permitting authorities work together with mercury dischargers in the watershed to collect data necessary to develop: o A TMDL, or o An analysis of sources and loading capacity similar to what a TMDL would provide, or o A water column translation of the fish tissue criterion for future permitting. One approach is for the permitting authority to invoke its authority under CWA section 308 (or comparable state authority).	FT alone	7.5.2.2
Additional requirements that may apply • Additional requirements for: POTWs with pretreatment programs; technology-based limits; anti-backsliding; permit documentation.	FT or WC	7.5.2.3
Mercury minimization plans (MMPs) This section provides guidance on appropriate MMPs.	FT	7.5.2.4

Notes:

[a] "Reasonable potential" refers to the reasonable potential to cause or contribute to an excursion above a numeric or narrative criterion for water quality. 40 CFR 122.44(d)(1)(i). NPDES permits for discharges with "reasonable potential" must include water quality-based effluent limits (WQBELs).

[b] As noted at the beginning of table 1d, this section refers to situations where neither a TMDL nor a water column translation is available at time of permit issuance. Where a TMDL has been developed, the WQBEL for that discharge must be consistent with the TMDL's wasteload allocation. Where a TMDL is not available at the time of permit discharge, but where a water column translation of the fish tissue criterion has been developed, or where site-specific data to do so are readily available, include a numeric WQBEL.

2 Introduction

2.1 What is the interest in mercury?

Mercury occurs naturally in the earth's crust and cycles in the environment as part of natural and human-induced activities. The amount of mercury mobilized and released into the biosphere has increased since the beginning of the industrial age. Most of the mercury in the atmosphere is elemental mercury vapor, which circulates in the atmosphere for up to a year and therefore can be widely dispersed and transported thousands of miles from sources of emission (USEPA 1997b). Most of the mercury in water, soil, sediments, plants, and animals is in the form of inorganic mercury salts and organic forms of mercury (e.g., methylmercury). Inorganic mercury salts, when bound to airborne particles, are readily removed from the atmosphere by precipitation and are also dry deposited. Even after mercury deposits, it commonly returns to the atmosphere, as a gas or associated with particles, and then redeposits elsewhere. As it cycles between the atmosphere, land, and water, mercury undergoes a series of complex chemical and physical transformations, many of which are not completely understood (USEPA 1997b).

This guidance focuses on an organic mercury compound known as methylmercury. Methylmercury most often results from microbial activity in wetlands, the water column, and sediments, and it is the form of mercury that presents the greatest environmental risks to human health (66 FR 1344; January 8, 2001). The methylation process and methylmercury bioaccumulative patterns are discussed in more detail in section 2.3.

2.1.1 What are the health effects of methylmercury?

Exposure to methylmercury can result in a variety of health effects in humans. Children that are exposed to low concentrations of methylmercury prenatally might be at risk of poor performance on neurobehavioral tests, such as those measuring attention, fine motor function, language skills, visual-spatial abilities, and verbal memory (NRC 2000; USEPA 2002a). Mercury and its compounds are listed as a "toxic" pollutant under section 307(a) of the Clean Water Act (see 40 CFR 401.15).

In 2000 the National Academy of Sciences (NAS)/National Research Council (NRC) reviewed the health studies on mercury (NRC 2000). EPA's assessment of the methylmercury reference dose (RfD) relied on the quantitative analyses performed by the NRC (USEPA 2002a). The RfD is an estimate (with uncertainty spanning perhaps an order of magnitude) of a daily exposure of the human population, including sensitive subgroups, that is likely to be without an appreciable risk of deleterious effects during a lifetime (USEPA 2002a). In its review of the literature, NRC found neurodevelopmental effects to be the most sensitive endpoints and appropriate for establishing a methylmercury RfD (NRC 2000).

On the basis of the NRC report, EPA established an RfD of 0.0001 mg/kg-day (0.0001 milligram of methylmercury per day for each kilogram of a person's body mass) (USEPA 2002a). EPA believes that exposures at or below the RfD are unlikely to be associated with an appreciable risk of deleterious effects. It is important to note, however, that the RfD does not define an exposure level corresponding to zero risk; mercury exposure near

or below the RfD could pose a very low level of risk that EPA deems nonappreciable. It is also important to note that the RfD does not define a bright line above which individuals are at risk of adverse effects (USEPA 2005a).

The primary route by which the U.S. population is exposed to methylmercury is through the consumption of fish containing methylmercury. The exposure levels at which neurological effects have been observed in children can occur through maternal consumption of fish (rather than high-dose poisoning episodes) (USEPA 2005a).

In 2005 the National Health and Nutrition Examination Survey (NHANES) published the results of a study of blood mercury levels in a representative sample of U.S. women of childbearing age (CDC 2005). The report data for the period 1999–2002 show that all women of childbearing age had blood mercury levels below 58 µg/L, a concentration associated with neurological effects in the fetus. These data show that 5.7 percent of women of childbearing age had blood mercury levels between 5.8 and 58 µg/L; that is, levels within an order of magnitude of those associated with neurological effects. Typical exposures for women of childbearing age were generally within two orders of magnitude of exposures associated with these effects, according to data from NHANES (CDC 2005; USEPA 2005a).

With regard to other health effects of methylmercury, some recent epidemiological studies in men suggest that methylmercury is associated with a higher risk of acute myocardial infarction, coronary heart disease, and cardiovascular disease in some populations (Salonen et al. 1995, as cited in USEPA 2001a). Other recent studies have not observed this association. The studies that have observed an association suggest that the exposure to methylmercury might offset the beneficial effects of fish consumption (USEPA 2005a). There also is some recent evidence that exposures to methylmercury might result in genotoxic or immunotoxic effects ([Amorim et al. 2000; ATSDR 1999; Silva at al. 2004], as cited in USEPA 2005a). Other research with less corroboration suggests that reproductive, renal, and hematological impacts could be of concern. There are insufficient human data to evaluate whether these effects are consistent with methylmercury exposure levels in the U.S. population (USEPA 2005a).

Deposition of mercury to waterbodies can also have an adverse impact on ecosystems and wildlife. Plant and aquatic life, as well as birds and mammalian wildlife, can be affected by mercury exposure; however, overarching conclusions about ecosystem health and population effects are difficult to make. Mercury contamination is present in all environmental media; aquatic systems experience the greatest exposures because of bioaccumulation. *Bioaccumulation* refers to the net uptake of a contaminant from all possible pathways. It includes the accumulation that might occur by direct exposure to contaminated media, as well as uptake from food. Elimination of methylmercury from fish is so slow that long-term reductions of mercury concentrations in fish are often due to growth of the fish (“growth dilution“), whereas other mercury compounds are eliminated relatively quickly. Piscivorous avian and mammalian wildlife are exposed to mercury mainly through consuming contaminated fish, and as a result they accumulate mercury to levels greater than those in their prey (USEPA 1997a).

EPA's mercury Web site, at http://www.epa.gov/mercury, provides a broad range of information about mercury, including a full discussion of potential human health and ecosystem effects.

2.1.2 How frequent are the environmental problems?

As of the 2008 listing of impaired waters (i.e.: water not attaining water quality standards) under section 303(d) of the clean Water Act, 43 states and Puerto Rico reported at least one waterbody as impaired due to mercury, and more than 8,800 specific waterbodies were listed as impaired due to mercury, either solely or in combination with other pollutants. All states have numeric criteria for mercury. About seven states, plus Washington D.C. and two territories have adopted a fish tissue criterion for methylmercury. Once additional states, tribes and territories begin to adopt EPA's recommended fish tissue criterion, the number of waterbodies listed as impaired for methylmercury is expected to increase since the revised criterion is more stringent than the water concentration criteria most states currently have in their water quality standards.

In 2001 EPA mapped concentrations of mercury in fish tissue from fish collected from waterbodies all over the country (i.e., not limited to the waters identified by the states as impaired) and compared them to the 2001 national recommended water quality criterion, 0.3 mg methylmercury/kg fish tissue wet weight. These data were not randomly or systematically collected, but rather reflect fish tissue information that states had collected as part of their fish consumption advisory programs. Approximately 40 percent of the watershed-averaged fish tissue concentrations exceeded 0.3 mg methylmercury/kg fish tissue wet weight (USEPA 2001b).

Figure 1 shows fish tissue mercury concentrations averaged by watershed (by 8-digit hydrologic unit code, or HUC).

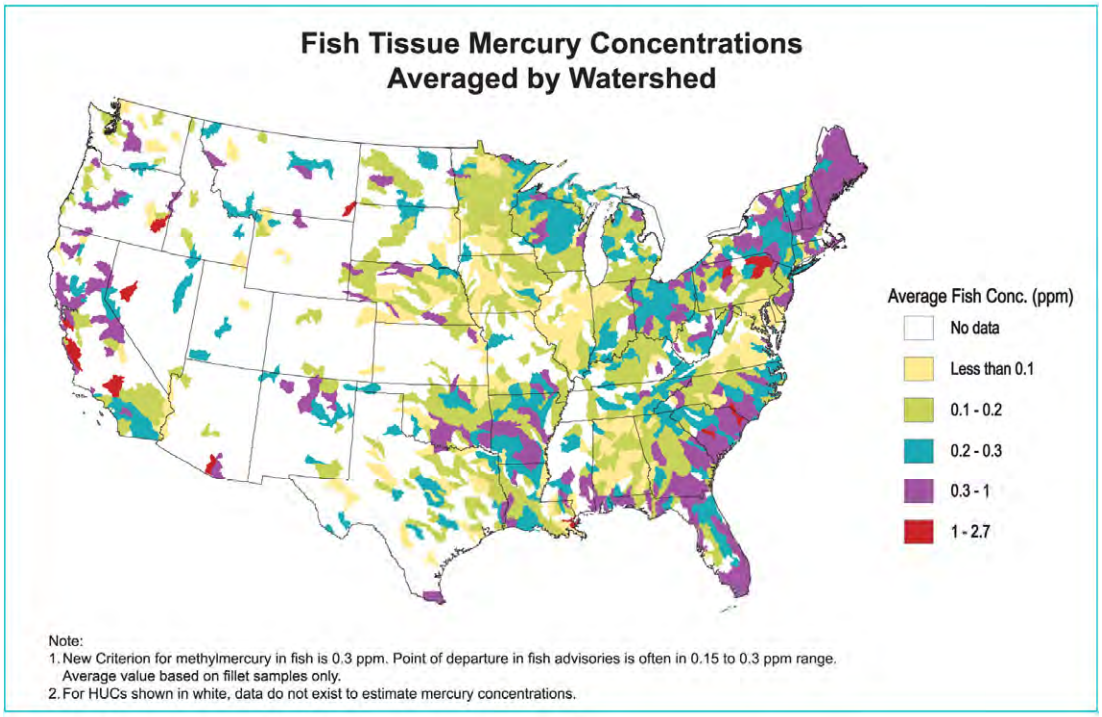


Figure 1. Average fish tissue concentrations by HUC watershed (USEPA 2005a).

In EPA's *Environmental Monitoring and Assessment Project (EMAP) Western Streams and Rivers Statistical Study* (USEPA 2005b), 626 streams and rivers were sampled in 12 states of the western United States. Mercury was detected at 100 percent of sites and samples in the study. The 0.3 mg/kg criterion (equivalent to 0.3 parts per million, ppm) was exceeded in 56.8 percent of waters surveyed, which represent 20–30 percent of all western rivers (Peterson et al. 2007). Results from the 2009 National Lake Fish Tissue Study, a statistically-based survey conducted by EPA, showed that 49% of the sampled population of lakes (76,559 lakes in the lower 48 states with surface areas greater than or equal to 1 hectare or about 2.5 surface acres) had mercury concentrations that exceeded the 0.3 ppm tissue-based mercury criterion (USEPA 2009b).

As of December 2008, 50 states, 1 territory, and 3 tribes had issued fish consumption advisories[1] for mercury covering 16.8 million lake acres and 1.3 million river miles (figure 2). Twenty-seven states had issued advisories for mercury in all freshwater lakes and rivers in the state, 13 states had statewide advisories for mercury in their coastal waters and one state had a deep sea advisory (USEPA 2009a). The thresholds for the levels of mercury in fish that trigger the issuance of an advisory for women of childbearing age vary among the states and authorized tribes, but generally range from 0.07 to 1 ppm, with most threshold values in the range of 0.1 to 0.3 ppm.

Although states, territories, tribes, and local governments continue to issue new fish advisories and most new fish advisories involve mercury, EPA believes that the increase in advisories is a result of increased monitoring and assessment of previously untested waters rather than increased domestic releases of mercury or increased levels or frequency of contamination. In fact, U.S. releases of mercury to the air have declined by more than 58 percent between 1990 and 2005 (USEPA 2008b).

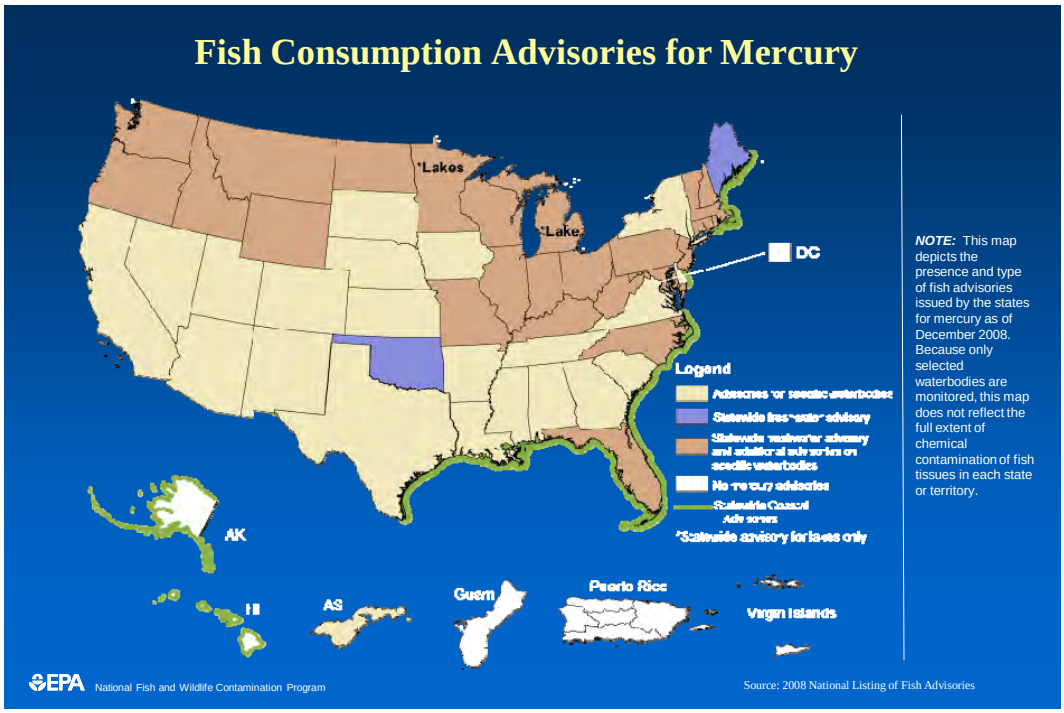


Figure 2. Fish Consumption Advisories for Mercury 2008 (USEPA 2009a).

[1] States and tribes issue their advisories and guidelines voluntarily and have flexibility in which criteria they use and how they collect data. As a result, there are significant variations in the numbers of waters tested, the pollutants tested for, and the threshold for issuing advisories. Based on self-reporting, the national trend is for states to monitor different waters each year, generally without retesting waters monitored in previous years. Note that EPA does not issue fish advisories; states and tribes issue advisories (with the exception of national advisories, regional advisories, and Superfund-related advisories). EPA issues guidance on the level of contaminants in fish, which states and tribes may use in issuing their advisories.

2.2 What are the sources of mercury in fish?

Mercury is emitted from both natural and anthropogenic sources. Its residence time in the atmosphere is much longer than that of most other metals because mercury can circulate for up to a year (USEPA 1997b). Such mobility enables elemental mercury to disperse and be transported over thousands of miles from likely sources of emission, across regions, and around the globe. As a result, the mercury detected in fish in U.S. surface waters is from both U.S. and international sources (USEPA 2005c). EPA estimates that approximately 83 percent of the atmospheric mercury deposited on land and water in the country is from a combination of sources outside the United States and Canada, as well as from natural and re-emitted sources. EPA's current air quality modeling indicates a substantial variation across the country: domestic sources influence mercury deposition much more in the East, and global sources are a more significant contributor to mercury deposition in the West, where relatively few domestic sources exist. This estimate was based on a modeling assessment of the atmospheric fate, transport, and deposition of mercury conducted by EPA for the Clean Air Mercury Rule[2] (USEPA 2005d).

Natural sources of mercury include geothermal emissions from volcanoes and crustal degassing in the deep ocean, as well as dissolution of mercury from other geologic sources (Rasmussen 1994). Anthropogenic sources of mercury in the United States include combustion (e.g., utility boilers; municipal waste combustors; commercial/industrial boilers; hospital, medical, and infectious waste incinerators), manufacturing sources (e.g., chlor-alkali and cement manufacturers), and mining (USEPA 1997b).

U.S. anthropogenic emissions of mercury to the air have declined more than 58 percent from the passage of the 1990 Clean Air Act (CAA) Amendments to 2005 (most recent data available). These amendments provided EPA new authority to reduce emissions of mercury and other toxic pollutants to the air. In 1990 more than two-thirds of U.S. human-caused mercury emissions came from just three source categories: coal-fired power plants; municipal waste combustion; and hospital, medical, and infectious waste incineration (figure 4, section 6.2.2.1). Regulations were issued in the 1990s to control mercury emissions from waste combustion. In addition, actions to limit the use of mercury—most notably voluntary and Congressional action to limit the use of mercury in batteries and EPA regulatory limits on the use of mercury in paint—contributed to the reduction of mercury emissions from waste combustion during the 1990s by reducing the mercury content of waste. Regulation of mercury emissions from chlorine production facilities that use mercury cells and regulation of industrial boilers will further reduce emissions of mercury.[3]

[2] On February 8, 2008, the D.C. Circuit Court of Appeals vacated the Section 112(n) Revision Rule and the Clean Air Mercury Rule.

[3] Rules controlling mercury emissions, which implement the 1990 CAA amendments, include standards for municipal waste combustors (40 CFR part 60, subpart Da, and parts 72 and 75); standards for hospital, medical, and infectious waste incinerators (40 CFR part 60, subpart Ce); standards for chlor-alkali plants (40 CFR part 63, subpart IIIII); standards for existing and new hazardous waste-burning incinerators (40 CFR 63.1203 [a][2] and [b][2]); standards for existing and new hazardous waste-burning cement kilns (40 CFR 63.1204 [a][2] and [b][2]); and standards for existing and new hazardous waste-burning lightweight aggregate kilns (40 CFR 63.1205 [a][2] and [b][2]). See also section 8.3 of this document.

At present, the largest single source of anthropogenic mercury emissions to the air in the country is coal-fired power plants. Mercury emissions from U.S. power plants are estimated to account for about one percent of total global mercury emissions (70 FR 15994; March 29, 2005). In May 2005, EPA adopted the Clean Air Act Section 112(n) Revision Rule and the Clean Air Mercury Rule (CAMR). CAMR regulated mercury emissions from coal-fired utilities. On February 8, 2008, the D.C. Circuit Court of Appeals vacated the Section 112(n) Revision Rule and CAMR. EPA is developing air toxics emissions standards for power plants under Clean Air Act (Section 112(d). EPA currently intends to propose and finalize air toxics standards for coal- and oil-fired electric generating units by the end of 2011. Point sources of mercury discharging into waters are also regulated by NPDES permits. Chlor-alkali facilities are subject to effluent guidelines that impose treatment levels reflective of the Best Available Technology Economically Achievable (40 CFR part 415). All NPDES permits must ensure that permitted discharges achieve water quality standards (40 CFR 122.44(d)). Nonpoint source runoff is not regulated under federal regulations, but to the extent that these sources cause a water to exceed its water quality standards, states will develop TMDLs that identify the necessary reductions from these sources for achieving the water quality standards.

Anthropogenic emissions, however, are only one part of the mercury cycle. Releases from human activities today add to the mercury reservoirs that already exist in land, water, and air, both naturally and as a result of previous human activity.

2.3 How does methylmercury get into fish and shellfish?

Mercury is widely distributed in the environment. Understanding the distribution and cycling of mercury among the abiotic (nonliving) and biotic (living) compartments of aquatic ecosystems is essential to understanding the factors that govern methylmercury uptake in fish and shellfish tissue. The following is a synopsis of the current understanding of mercury cycling in the environment.

Mercury occurs naturally in the environment as several different chemical species. Most mercury in the atmosphere (95–97 percent) is present in a neutral, elemental state, Hg^0 (Lin and Pehkonen 1999). In water, sediments, and soils, most mercury is found in the oxidized, divalent state, Hg^{II} (Morel et al. 1998). A small fraction of this pool of divalent mercury is transformed by microbes into methylmercury (CH_3Hg^{II}) (Jackson 1998). Methylmercury is retained in fish tissue and is the only form of mercury that biomagnifies in aquatic food webs (Kidd et al. 1995). Transformations among mercury species within and between environmental media result in a complicated chemical cycle.

The relative contributions of local, regional, and long-range sources of mercury to fish mercury levels in a given waterbody are strongly affected by the speciation of natural and anthropogenic emission sources. Elemental mercury is oxidized in the atmosphere to form the more soluble mercuric ion, Hg^{II} (Schroeder et al. 1989). Particulate and reactive gaseous phases of Hg^{II} are the principal forms of mercury deposited onto terrestrial and aquatic systems because they are more efficiently scavenged from the atmosphere through wet and dry deposition than is Hg^0 (Lindberg and Stratton 1998). Because Hg^{II} species or reactive gaseous mercury (RGM) and particulate mercury (Hg_p) in the atmosphere tend to be deposited more locally than Hg^0, differences in the species of

mercury emitted affect whether the mercury is deposited locally or travels longer distances in the atmosphere (Landis et al. 2004).

A portion of the mercury deposited in terrestrial systems is re-emitted to the atmosphere. On soil surfaces, sunlight might reduce deposited Hg^{II} to Hg^{0}, which might then escape back to the atmosphere (Carpi and Lindberg 1997, Frescholtz and Gustin 2004, Scholtz et al. 2003). Significant amounts of mercury can be co-deposited to soil surfaces in throughfall and litterfall of forested ecosystems (St. Louis et al. 2001), and exchange of gaseous Hg^{0} by vegetation has been observed (e.g., Gustin et al. 2004). Hg^{II} has a strong affinity for organic compounds such that inorganic mercury in soils and wetlands is predominantly bound to dissolved organic matter (Mierle and Ingram 1991). Concentrations of methylmercury in soils are generally very low. In contrast, wetlands are areas of enhanced methylmercury production and account for a significant fraction of the external methylmercury inputs to surface waters that have watersheds with a large portion of wetland coverage (e.g., St. Louis et al. 2001).

In the water column and sediments, Hg^{II} partitions strongly to silts and biotic solids, sorbs weakly to sands, and complexes strongly with dissolved and particulate organic material. Hg^{II} and methylmercury sorbed to solids settle out of the water column and accumulate on the surface of the benthic sediment layer. Surficial sediments interact with the water column through resuspension and bioturbation. The amount of bioavailable methylmercury in water and sediments of aquatic systems is a function of the relative rates of mercury methylation and demethylation. In the water, methylmercury is degraded by two microbial processes and sunlight (Barkay et al. 2003; Sellers et al. 1996). Mass balances for a variety of lakes and coastal ecosystems show that *in situ* production of methylmercury is often one of the main sources of methylmercury in the water and sediments (Benoit et al. 1998; Bigham and Vandal 1994; Gbundgo-Tugbawa and Driscoll 1998; Gilmour et al. 1998; Mason et al. 1995). Changes in the bioavailability of inorganic mercury and the activity of methylating microbes as a function of sulfur, carbon, and ecosystem-specific characteristics mean that ecosystem changes and anthropogenic "stresses" that do not result in a direct increase in mercury loading to the ecosystem, but alter the rate of methylmercury formation, might also affect mercury levels in organisms (e.g., Grieb et al. 1990).

Dissolved Hg^{II} and methylmercury accumulate in aquatic vegetation, phytoplankton, and benthic invertebrates. Unlike Hg^{II}, methylmercury biomagnifies through each successive trophic level in the benthic and pelagic food chains such that mercury in predatory, freshwater fish is found almost exclusively as methylmercury (Bloom 1992; Watras et al. 1998). In fish, methylmercury bioaccumulation is a function of several uptake pathways (diet, gills) and elimination pathways (excretion, growth dilution) (Gilmour et al. 1998; Greenfield et al. 2001). Factors such as pH, length of the aquatic food chain, temperature, and dissolved organic carbon (DOC) can affect bioaccumulation (Ullrich et al. 2001). As a result, the highest mercury concentrations for a given fish species correspond to smaller, long-lived fish that accumulate methylmercury over their life span with minimal growth dilution (e.g., Doyon et al. 1998). In general, higher mercury concentrations are expected in top predators, which are often large fish relative to other species in a waterbody.

2.4 Why is EPA publishing this document?

In a January 8, 2001, *Federal Register* notice (66 FR 1344), EPA announced the availability of its recommended water quality criterion for methylmercury. In that notice, EPA also stated that development of the associated implementation procedures and guidance documents would begin by the end of 2001. Therefore, EPA makes this guidance available to fulfill that commitment to assist states and authorized tribes to adopt into their water quality standards the recommendations set forth in *Water Quality Criterion for the Protection of Human Health: Methylmercury* (USEPA 2001a), or other water quality criteria for methylmercury where such other criteria are based on scientifically defensible methods.

This nontraditional approach—developing a water quality criterion as a fish and shellfish tissue value—raises several implementation questions on both technical and programmatic fronts. Development of water quality standards, NPDES permits, and TMDLs presents many challenges because these activities have usually been based on a water concentration (e.g., as a measure of mercury levels in effluent or receiving waters). This guidance addresses issues associated with states' and authorized tribes' adoption of the new water quality criterion into their water quality standards programs and implementation of the revised water quality criterion in TMDLs and NPDES permits. Furthermore, because atmospheric deposition is a large source of mercury for many waterbodies, implementation of this criterion involves coordination across various media and program areas, which is also addressed in this guidance.

At this time, about seven states, plus Washington D.C. and two territories have adopted a fish tissue criterion for methylmercury with EPA approval. EPA expects that with the publication of this guidance, states and authorized tribes will include new or revised criteria for methylmercury in their waters as part of the next three year review of standards required by section 303(c) of the Clean Water Act. This expanded adoption of the 2001 methylmercury fish tissue criterion, together with a more sensitive method for detecting mercury in effluent and the water column and increased monitoring of previously unmonitored waterbodies, is expected to result in an increase in the number of waterbodies that states identify as impaired by mercury on CWA section 303(d) lists.

This guidance includes recommended approaches for relating a concentration of methylmercury in fish tissue to a concentration of mercury in ambient water (see chapter 3); a recommended approach for directly using the methylmercury tissue criterion as a basis for issuing NPDES permits (see chapter 7); and approaches that have been used in approved TMDLs for waterbodies impaired by mercury. This guidance includes examples of TMDL approaches for waterbodies where much of the mercury comes from atmospheric sources, as well as examples of TMDLs for waterbodies where the mercury

is predominantly from past mining activity. Finally, the guidance describes ongoing EPA efforts to address sources of mercury, such as programs under the CAA and pollution prevention activities.

EPA recognizes the complexity and comprehensive nature of this guidance. As is always the case when EPA issues technical guidance, EPA will provide outreach and technical assistance to states and authorized tribes in implementing this guidance.

2.5 What is the effect of this document?

This guidance document presents suggested approaches—but not the only technically defensible approaches—to criteria adoption and implementation. The guidance is not a substitute for applicable sections of the CWA or EPA's regulations; nor is it a regulation itself. Thus, it cannot impose legally binding requirements on EPA, states, authorized tribes, or the regulated community and may not apply to a particular situation. EPA, state, territorial, and tribal decision makers retain the discretion to adopt other scientifically defensible approaches that differ from this guidance. EPA may change this guidance in the future.

3 Water Quality Criteria and Standards Adoption

3.1 What must states and authorized tribes include as they adopt the methylmercury criterion?

3.1.1 What do the CWA and EPA's regulations require?

The CWA and EPA's regulations specify the requirements for adoption of water quality criteria into state or tribal water quality standards. States and authorized tribes must adopt water quality criteria[4] that protect designated uses. See CWA section 303(c)(2)(A). Water quality criteria must be based on a sound scientific rationale and must contain sufficient parameters or components to protect the designated uses (see 40 CFR 131.11). States and authorized tribes are required to review standards every three years and submit changes to EPA for approval.

Whenever they review or revise standards, states and authorized tribes are to adopt numeric criteria for all toxic pollutants for which EPA has established national recommended ambient water quality criteria (AWQC) and where the discharge or presence of these pollutants could reasonably interfere with the designated uses (see CWA section 303(c)(2)(B)). Mercury and related compounds are identified as toxic pollutants in EPA regulations (40 CFR 401.15) and EPA published a criterion under 304(a) for methylmercury in 2001. EPA issued guidance on how states and authorized tribes may comply with CWA section 303(c)(2)(B), which is now contained in the *Water Quality Standards Handbook: Second Edition* (USEPA 1994). This document provides three options for compliance:

- Option 1: States and authorized tribes may adopt statewide or reservation-wide numeric chemical-specific criteria for all toxic pollutants for which EPA has issued CWA section 304(a) criteria guidance.
- Option 2: States and authorized tribes may adopt numeric chemical-specific criteria for those stream segments where the state or tribe determines that the priority toxic pollutants for which EPA has issued CWA section 304(a) criteria guidance are present and can reasonably be expected to interfere with designated uses (e.g., a designated use of "fishing" is interfered with by nonattainment of the mercury water quality criterion).

[4] The term *water quality criteria* has two different definitions under the CWA. Under CWA section 304(a), EPA publishes recommended water quality criteria guidance that consists of scientific information regarding concentrations of specific chemicals or levels of parameters in water that protect aquatic life and human health. The 2001 methylmercury criterion is an example of a recommended section 304(a) criterion. States may use these recommended criteria as the basis for developing water quality standards. Water quality criteria are also elements of state water quality standards adopted under CWA section 303(c).

- Option 3: States or authorized tribes may adopt a chemical-specific translator procedure[5] that can be used to develop numeric criteria as needed.

EPA considers the 2001 methylmercury criterion a sound, scientifically based approach for meeting human health designated uses. In addition, this guidance addresses a range of complex technical issues and responds to the questions that states and authorized tribes have raised. Thus, EPA strongly encourages states and authorized tribes to adopt the 2001 methylmercury criterion or any sound, scientifically based approach for methylmercury or mercury, into their water quality standards at the upcoming triennial review of standards to fulfill the requirements of section 303(c) (2)(B) of the Clean Water Act and 40 CFR part 131. Numerical criteria for mercury in water, rather than fish tissue, published by EPA and in effect prior to 2001, may be included temporarily as part of revised mercury criteria at the next triennial review as provided for below.

3.1.2 What is the recommended form of the methylmercury criterion?

EPA's current recommended CWA section 304(a) water quality criterion for methylmercury is expressed as a fish[6] tissue concentration value (0.3 milligram methylmercury per kilogram of wet-weight fish tissue, or 0.3 mg/kg). With the publication of the fish tissue criterion, EPA withdrew the previous human health water quality criterion for mercury as the recommended section 304(a) water quality criterion for states and authorized tribes to use as guidance in adopting water quality standards (USEPA 2001c). These water column criteria, however, may be temporarily part of revised mercury criteria until the triennial review that follows the criterion adoption to help the transition in implementing the fish tissue criterion.

States and authorized tribes have several options for adopting a new or revised methylmercury criterion into their water quality standards. They may:

- Adopt the 2001 criterion or other scientifically defensible criterion as a fish tissue residue concentration, and implement it without water column translation; or
- Adopt a water column concentration, using the translation methodologies outlined in section 3.1.3.1, and implement it using traditional approaches; or
- Use a combination of the above approaches. For example, states and tribes could adopt a fish tissue criterion and implement it without water column translation for some or all waters, and translate the criterion to water column values for some or all waters.

Site-specific data for translating the fish tissue criterion to water column concentration, where needed, may take time to collect. Accordingly, states and authorized tribes may

[5] A *translator procedure* is simply the detailed process adopted by a state or authorized tribe, that explains how the state or authorized tribe will interpret its narrative criteria for toxics so that a quantifiable term can be used in assessment, permitting, and TMDL development. For example, a state or tribe could use EPA's water quality criteria as the means for interpreting its narrative criteria.

[6] The criterion applies to both finfish and shellfish. For purposes of simplifying language in this document, the term *fish* means both finfish and shellfish.

consider retaining their existing water column criteria, on a temporary basis, particularly for waters where there is a relatively high direct water input of mercury. In such a case, where the state has retained the existing water column criteria, permits must include both a limit based on the existing numeric water column criterion and other requirements based on the fish tissue criterion (see chapter 7).

Where a water column translation of the fish tissue criterion has been developed or where site-specific data to do so are readily available using one of the options in Section 3.1.3.1, states and authorized tribes should translate the fish tissue criterion, and implement using traditional approaches. If site-specific data are not available to translate, the state or authorized tribe may design data collection activities to obtain the necessary data. States and authorized tribes should focus data collection activities on water bodies where methylmercury impairments are high priorities for action because of high direct water inputs. EPA recommends that states and tribes not only focus on data collection but also on the development of translators for waters with high direct water inputs of mercury. Additionally, EPA recommends that states and tribes include such translators in their criterion implementation plans.

States and authorized tribes remain free not to use EPA's current recommendations, provided that their new or revised water quality criteria for methylmercury protect the designated uses and are based on a scientifically defensible methodology. In doing this, states and authorized tribes should consider bioaccumulation and local or statewide fish consumption. EPA will evaluate criteria submitted by states and authorized tribes case by case.

If states and authorized tribes decide to adopt the tissue criterion expressed as a fish tissue concentration without translating it to a traditional water column concentration, this decision will lead to choices on how to implement the tissue criterion. A state or authorized tribe could decide to develop TMDLs and to calculate WQBELs in NPDES permits directly without first measuring or calculating a BAF. This guidance provides options for such approaches in chapters 6 and 7.

EPA does not require states and tribes to translate the fish tissue criterion into water column criteria. For waters with relatively high direct water inputs of mercury (mercury from point sources and nonpoint sources other than air deposition), EPA does recommend developing TMDLs, an analysis of sources and loading capacity similar to what would be provided in a TMDL, or a water column translation of the fish tissue criterion, to provide important information for developing appropriate permit limits. See section 7.5.2.2 for a further discussion of this situation.

3.1.2.1 Developing a methylmercury criterion implementation plan

Regardless of the approach a state decides to use to implement its criterion, EPA encourages states and authorized tribes to develop a methylmercury criterion implementation plan to ensure environmentally protective and effective administration of all water quality related programs with respect to methylmercury. Developing a methylmercury implementation plan can facilitate adoption of the tissue-based criterion and provide transparency on state or tribal approaches to the numerous implementation issues associated with this type of criterion. This benefits not only the state or tribe but the regulated community and the public.

Examples of potential implementation issues the plan could cover include criterion adoption into the water quality standards (e.g., tissue or water column value with translators, BAF development methods), reasonable potential and permitting decisions, ambient monitoring strategies, and impairment determinations.

Developing an implementation plan could also facilitate subsequent regulatory decisions. Working with stakeholders and the public to develop an appropriate implementation plan concurrent with adoption of a tissue-based criterion could facilitate subsequent implementation decisions (e.g., application of the criterion in the context of 303(d) listing decisions or NPDES permitting actions) and decrease the likelihood of legal challenges.

It may be most useful to states and tribes to develop such an implementation plan prior to the adoption of the fish tissue criterion. States and tribes could propose draft plans when they are developing updates or revisions to their water quality standards. Additionally, EPA encourages states and tribes to take public comment on their draft plan during the time when the state or tribe is proposing to adopt the fish tissue criterion.

If a state or tribe develops a methylmercury implementation plan during adoption of its criterion, the state or tribe should submit the plan to EPA with the state's new criterion. Although the plan itself is not subject to EPA review and approval, the plan could facilitate EPA's review of the new criterion.

3.1.2.2 Why is the fish tissue concentration criterion recommended?

EPA recommends that when states and authorized tribes adopt new or revised methylmercury water quality criteria, they adopt the criteria in the form of a fish tissue methylmercury concentration. This is the preferred form for the following reasons:

- A criterion expressed as a fish tissue concentration is closely tied to the "fishable" designated use goal applied to nearly all waterbodies in the United States.
- A fish tissue concentration value is expressed in the same form (fish tissue) through which humans are exposed to methylmercury.
- A fish tissue concentration value is more consistent with how fish advisories are issued.
- At environmentally relevant concentrations, methylmercury is currently easier to detect in fish tissue than in water samples.

3.1.2.3 How is the fish tissue concentration criterion calculated?

The derivation of a methylmercury water quality criterion uses a human health toxicological risk assessment (e.g., a reference dose [RfD]), exposure data (e.g., the amount of pollutant ingested, inhaled, or absorbed per day), and data about the target population to be protected. The methylmercury fish tissue residue criterion (TRC) for the protection of human health is calculated as:

$$TRC = \frac{BW \times (RfD - RSC)}{\sum_{i=2}^{4} FI} \qquad \text{(Equation 1)}$$

Where:

TRC = fish tissue residue criterion (in mg/kg) for freshwater and estuarine fish and shellfish

RfD = reference dose (based on noncancer human health effects); for methylmercury, it is 0.1 µg/kg body weight/day

RSC = relative source contribution (subtracted from the RfD to account for methylmercury in marine fish consumed[7]), estimated to be 0.027 µg/kg body weight/day

BW = human body weight (default value of 70 kg for adults)

FI = fish intake at trophic level (TL)*i* (*i* = 2, 3, 4); total default intake of uncooked freshwater and estuarine fish is 17.5 g fish/day for the general U.S. adult population[8]

This equation and all values used in the equation are described in *Water Quality Criterion for the Protection of Human Health, Methylmercury* (USEPA 2001a). This equation is essentially the same equation used in the 2000 Human Health Methodology (USEPA 2000b) to calculate a water quality criterion for a pollutant that may cause noncancerous health effects. Here, it is rearranged to solve for a protective concentration in fish tissue rather than in water. Thus, it does not include a BAF or drinking water intake value (methylmercury exposure from drinking water is negligible (USEPA 2001c)).

When all the numeric values are put into the generalized equation, the TRC of 0.3 mg methylmercury/kg fish is the concentration in fish tissue that should not be exceeded on the basis of a consumption rate of 17.5 g fish/day of freshwater or estuarine fish.

EPA encourages states and authorized tribes to collect, as quickly as possible, local or regional data to modify the fish consumption rate rather than using the default values if the state or authorized tribe believes that such a fish consumption rate would be more appropriate for its target population. This gives states and tribes the flexibility to develop criteria that provide additional protection appropriate for highly exposed populations that may be at greater risk than the general population protected by the 304(a) criterion (USEPA 2000b). Where states do not have site-specific data, but intend to collect this

[7] The RSC accounts for exposures from all anticipated sources so that the entire RfD is not apportioned to freshwater/estuarine fish and shellfish consumption alone. In the assessment of human exposure in the methylmercury water quality criterion document, EPA found that human exposures to methylmercury were negligible except from freshwater/estuarine and marine fish. Therefore, in developing the criterion on the basis of consumption of freshwater/estuarine fish, EPA subtracted the exposure due to consumption of marine fish. See 66 FR 1354–1355; January 8, 2001.

[8] The consumption rate value of 17.5 grams uncooked fish per day is the 90th percentile of freshwater and estuarine fish consumed by the public according to the *1994–96 Continuing Survey of Food Intakes by Individuals* (USEPA 2000a). EPA uses this value as the default consumption rate in development of water quality criteria. The default trophic level values for the general population are 3.8 g fish/day for TL2, 8.0 g fish/day for TL3, and 5.7 g fish/day for TL4. The rationale behind the selection of this value is described in the Human Health Methodology (USEPA 2000b).

data over time to develop a more appropriate criterion, states should use EPA's default fish consumption rate on a temporary basis to be able to adopt and implement the fish tissue criterion in a timely manner.

The TRC value is not based on any default breakout of fish consumption by trophic level.The trophic levels assigned to the fish consumption value should reflect those that each target population consumes. For assessing impairment or attainment of the TRC, a state or authorized tribe may choose to assign the TRC value to only trophic level 4 or to the highest trophic level consumed. This approach is conservative in that it assumes that all fish consumed are at the highest trophic level, and it will likely protect most, if not all, populations at an uncooked freshwater or estuarine fish consumption rate of 17.5 grams/day. If a state or authorized tribe wishes to calculate the TRC value on the basis of consumption at each trophic level for monitoring and compliance purposes, it would first determine consumption patterns at each trophic level for the target population(s). (For information on determining consumption patterns, see chapter 4.) This approach might be more precise and is less likely to be overprotective; however, developing it could be resource-intensive.

3.1.3 What approaches should states or authorized tribes consider when developing a water column concentration criterion?

As described in section 3.1.2 above, there may be situations where it is appropriate to adopt a criterion expressed as a water column concentration. EPA recognizes that a fish tissue residue water quality criterion is new to states and authorized tribes and might pose implementation challenges for traditional water quality programs. Water quality standards, water quality-based effluent limits[9] (WQBELs), total maximum daily loads (TMDLs), and other activities generally employ a water column value. This section provides information for states and authorized tribes that decide to adopt a water concentration criterion derived from a fish tissue criterion.

Alternatively, a state or authorized tribe may decide to adopt a fish tissue criterion with a site-specific procedure for translating the tissue criterion to a water column concentration. Because methylmercury bioaccumulation can vary substantially from one location to another, this option allows for the tissue criterion to be translated to a water concentration using site-specific information on methylmercury bioaccumulation (i.e., site-specific BAFs). Administratively, this option might be more efficient compared to adopting a water concentration criterion for an entire state or tribal jurisdiction or adopting or approving site-specific criteria on an individual waterbody basis. Approaches for translating a tissue concentration-based criterion to a water concentration are provided in the following section (section 3.1.3.1).

Developing a water column translation of the fish tissue criterion requires assessment of methylmercury bioaccumulation at an appropriate geographic scale. The uncertainty associated with differential bioaccumulation of methylmercury across sites within a state or tribal jurisdiction will be embedded in the state or tribal water-based criterion.

[9] A WQBEL is a requirement in an NPDES permit that is derived from, and complies with, all applicable water quality standards and is consistent with the assumptions and requirements of any approved wasteload allocation (see 40 CFR 122.44(d)(1)(vii)).

Reducing such uncertainty is one of the primary reasons EPA chose to express its national recommended criterion for methylmercury as a tissue concentration rather than as a water concentration.

To express the methylmercury tissue concentration-based criterion as a water concentration, a state or authorized tribe would translate the methylmercury criterion concentration in fish tissue to methylmercury concentrations in the water column. To accomplish this, the state or authorized tribe would develop BAFs. In the 2001 *Federal Register* notice of the methylmercury criterion, EPA identified three different possible approaches for developing a BAF. These approaches are discussed in more detail in section 3.1.3.1. The basic equations used in developing a water column criterion are presented below, and additional discussion of calculating BAFs is presented in the following section.

The following equation may be used to translate the tissue concentration-based human health AWQC to a water concentration-based methylmercury criterion using a BAF as

$$AWQC = TRC / BAF \qquad \text{(Equation 2)}$$

Where:

AWQC = water concentration-based ambient water quality criterion for methylmercury in milligrams per liter (mg/L)
TRC = tissue residue concentration; the water quality criterion for methylmercury in fish tissue in mg/kg
BAF = bioaccumulation factor for trophic levels 2, 3, and 4, weighted on the basis of fish consumption rates for each trophic level in liters per kilogram (L/kg)

The BAF is the ratio of the concentration of the chemical in the appropriate tissue of the aquatic organism and the concentration of the chemical in ambient water at the site of sampling. BAFs are trophic-level-specific. EPA recommends that they be derived from site-specific, field-measured data as

$$\text{BAF} = \frac{C_t}{C_w} \qquad \text{(Equation 3)}$$

Where:

BAF = bioaccumulation factor, derived from site-specific field-collected samples of tissue and water in L/kg
Ct = concentration of methylmercury in fish tissue in mg/kg, wet tissue weight
Cw = concentration of methylmercury in water in mg/L

When such data are unavailable, other approaches for deriving BAFs may be used, as outlined in section 3.1.3.1.

In the calculation to derive an AWQC as a water column concentration, the BAFs for the different trophic levels are combined to provide a weighted BAF value. For example, if a

state wants to protect a population that eats on average 17.5 grams per day of uncooked fish from a waterbody, and 75 percent of the fish eaten are in trophic level 4 and 25 percent of the fish eaten are in trophic level 3, the weighted BAF would be the sum of 0.25 times the trophic level 3 BAF and 0.75 times the trophic level 4 BAF. Section 3.2.1.2 provides guidance on estimating fish intake rates.

3.1.3.1 How is the methylmercury fish tissue concentration translated to a water concentration?

Should a state or authorized tribe decide to translate the methylmercury fish tissue criterion into a water column concentration, it would assess the extent to which methylmercury is expected to bioaccumulate in fish tissue for the site(s) of interest. Assessing and predicting methylmercury bioaccumulation in fish is complicated by a number of factors that influence bioaccumulation. These factors include the age or size of the organism; food web structure; water quality parameters such as pH, DOC, sulfate, alkalinity, and dissolved oxygen; mercury loadings history; proximity to wetlands; watershed land use characteristics; and waterbody productivity, morphology, and hydrology. In combination, these factors influence the rates of mercury bioaccumulation in various—and sometimes competing—ways. For example, these factors might act to increase or decrease the delivery of mercury to a waterbody, alter the net production of methylmercury in a waterbody (through changes in methylation and/or demethylation rates), or influence the bioavailability of methylmercury to aquatic organisms. Although bioaccumulation models have been developed to address these and other factors for mercury, their broad application can be limited by the site- or species-specific nature of many of the factors that influence bioaccumulation and by limitations in the data parameters necessary to run the models.

The bioaccumulation of nonionic organic chemicals[10] such as methylmercury can also be affected by a number of these same physicochemical factors (e.g., loading history, food web structure, dissolved oxygen, DOC). However, a substantial portion of the variability in bioaccumulation for nonionic organic chemicals can be reduced by accounting for lipid content in tissues and organic carbon content in water and "normalizing" BAFs using these factors (Burkhard et al. 2003; USEPA 2003). Normalizing to the age or size (length, weight) of fish has been shown to reduce variability in measures of bioaccumulation (Brumbaugh et al. 2001; Glass et al. 2001; Sonesten 2003; Sorensen et al. 1990; Wente 2004).

The United States Geological Survey (USGS) developed a procedure called the National Descriptive Model for Mercury in Fish Tissue (NDMMF) (Wente 2004). This model provides a translation factor to convert a mercury concentration taken from one species/size/sample method to an estimated concentration for any other user-predefined species/size/sample method.

[10] Nonionic organic compounds are those organic compounds that do not ionize substantially when dissolved in water and therefore are more likely to associate with sediment compounds, lipids, or other compounds in water (USEPA 2000b).

Mercury Terminology

For the purposes of this document, the following definitions apply:

Mercury (or total mercury): The sum of all forms of mercury, including methylmercury, other organic forms, inorganic, and elemental mercury. All of these are toxic, and inorganic and elemental mercury can be methylated in the environment.

Methylmercury: The organic form of mercury, that bioaccumulates in the food chain. (Other organic forms of mercury exist, but exposure to them through environmental pathways is not significant.)

Dissolved mercury (or filtered mercury): The portion of mercury that passes through a filter.

Dissolved methylmercury (or filtered methylmercury): The portion of methylmercury which passes through a filter.

Total recoverable mercury (or unfiltered mercury): The dissolved portion plus the particulate portion of mercury in a water sample.

Total recoverable methylmercury (or unfiltered methylmercury): The dissolved portion plus the particulate portion of methylmercury in a water sample.

Taking into account the previous discussion, EPA has outlined in this document three different approaches that could be considered for relating a concentration of methylmercury in fish tissue to a concentration of methylmercury in ambient water, should a state decide to develop or implement its standard in this manner:

1. Use site-specific methylmercury BAFs derived from field studies.
2. Use a scientifically defensible bioaccumulation model.
3. Where appropriate, use BAFs derived using the results of field studies that are not site-specific. Appropriate situations for using such BAFs include waters where direct water inputs are relatively high and where ambient fish tissue data are unavailable, where deriving site-specific, field-measured BAFs is not feasible, or where using a model is not feasible. Such BAFs may include the draft national BAFs presented in appendix A of Water Quality Criterion for the Protection of Human Health: Methylmercury (USEPA 2001a) and discussed in more detail below. Alternatively, BAFs may be derived using other approaches, such as a combination of national and site-specific data in conjunction with other, non-site-specific data, to create better estimates.

Of these approaches, 1 and 2 are preferred over 3. Because of the significant uncertainties inherent in non-site-specific estimates of BAFs (including the draft national BAFs), they should be used as defaults only in limited circumstances such as:

- When a state determines that use of the draft national BAFs are appropriate (for example, where direct water inputs are relatively high, where no other data are available to derive site-specific field-measured BAFs, and use of an appropriate BAF model is not feasible)
- When a state can show that such BAFs are appropriate for its situation (e.g., a state has data or analyses that demonstrate that the draft national BAFs would be appropriate)

- As an interim approach until more appropriate BAFs can be developed using other data and/or an alternate approach

The reasons for preferring approaches 1 and 2 are discussed in more detail below. However, the hierarchy assigned to the approaches is not intended to be inflexible. For example, in some cases, the site-specific information available may be so limited in quality or quantity that BAFs derived using other data may be preferable. In other cases, there might be enough site-specific information to indicate that the local conditions approximate the draft national values.

In situations where the state or tribe has some data available on fish tissue and water column levels in its jurisdiction, but data are insufficient to support broad development of site-specific translations, the state or tribe may be able to use these data in combination with an evaluation of the draft national BAFs to help develop water column translations. For example, California's Office of Environmental Health Hazard Assessment compiled mercury concentration data for water and biota, and calculated state-specific BAFs for different types of waters and different trophic levels. The office found enough similarities between the state-specific BAFs and EPA's draft national BAFs that it recommended using EPA's draft national values as an interim approach until more complete state-specific data becomes available (Sanborn and Brodberg 2006). The state is in the process of deciding whether to adopt this approach.

If the state or tribe chooses to derive BAFs using the third approach above, the state or tribe should provide an accompanying rationale that acknowledges an understanding of the potential limitations of the approach.

Developing site-specific data to support approaches 1 and 2 can be facilitated by efforts involving stakeholders, states, and authorized tribes. Developing site-specific data is one possible approach EPA recommends permitting authorities consider to help develop NPDES permits in watersheds where mercury loadings from point sources are relatively high. See section 7.5.2.2.

3.1.3.1.1 Site-specific bioaccumulation factors derived from field studies

The use of site-specific BAFs based on data obtained from field-collected samples of tissue from aquatic organisms that people eat and water from the waterbody of concern—referred to as a "field-measured site-specific BAF"—is the most direct and most relevant measure of bioaccumulation. This approach is consistent with EPA's bioaccumulation guidance contained in the 2000 Human Health Methodology (USEPA 2000b) and the Technical Support Document for developing national BAFs (USEPA 2003). Although a BAF is actually a simplified form of a bioaccumulation model, the field-measured site-specific BAF approach is discussed separately here because of its widespread use and application.

A field-measured site-specific BAF is derived from measurements of methylmercury concentrations in tissues of aquatic organisms and the ambient water they inhabit. Because the data are collected from a natural aquatic ecosystem, a field-measured BAF reflects an organism's exposure to a chemical through all relevant exposure routes (e.g., water, sediment, diet). Although a BAF can be measured for the aggregate of fish in a location, site-specific BAFs are often specific to trophic level and species of fish. The BAF can also be measured based on a predatory indicator species with a high propensity

for bioaccumulation, such as largemouth bass. A field-measured site-specific BAF also reflects biotic and abiotic factors that influence the bioavailability and metabolism of a chemical that might occur in the aquatic organism or its food web at a given location. By incorporating these factors, field-measured site-specific BAFs account for the actual uptake and accumulation of the chemical.

States and authorized tribes should exercise caution, however, in developing a site-specific BAF for a migratory fish because its exposure to methylmercury occurred in part in areas other than where the fish was caught and therefore might not accurately predict the water column mercury concentrations associated with the fish tissue concentration of mercury. States and tribes should consider the life history of the migratory fish and the consumption patterns of the local population when considering BAFs for migratory species. States and tribes should also review how the applicable RSC considers migratory fish when considering including those species in BAF calculations (see section 3.2.1.1).

For the purposes of developing a criterion expressed as a water concentration, states and authorized tribes should calculate the BAF as the ratio of the concentration of methylmercury in the tissue of aquatic organisms that people eat to the concentration of methylmercury in water[11] (Equation 3). To predict the corresponding methylmercury concentration in water for a site, the tissue-based methylmercury criterion would then be divided by the site-specific BAF (Equation 2). Using the site-specific BAF approach assumes that at steady state, the accumulation of methylmercury by the aquatic organism varies in proportion to the methylmercury concentration in the water column.

As an example, California is currently employing a site-specific BAF approach in its Central Valley Region. In this approach, the state evaluated graphs of average concentrations of methylmercury in water and the corresponding concentrations in fish at multiple sites in a watershed. Researchers found statistically significant, positive relationships between concentrations of unfiltered methylmercury in water and in various trophic levels of the aquatic food chain (Slotton et al. 2004). California linearly regressed fish tissue methylmercury concentrations for specific trophic level (TL) 3 and 4 fish against aqueous methylmercury concentrations ($P < 0.001$, $R^2 = 0.98$, and $P < 0.01$, $R^2 = 0.9$, respectively) and determined methylmercury concentrations in unfiltered water that correspond to the fish tissue criteria used in the TMDL analyses (0.15 ng/L for TL3 fish and 0.14 ng/L for TL4 fish) (Central Valley Water Board 2005). California assumed that sites that fit in a statistically significant regression have similar processes controlling methylmercury accumulation. In other words, site-specific BAFs for such sites are nearly identical.

Strengths associated with using a site-specific BAF approach include simplicity, widespread applicability (i.e., site-specific BAFs can be derived for any waterbody, fish species, and the like), and that the net effects of biotic and abiotic factors that affect

[11] Although BAFs are sometimes calculated to represent the relationship between methylmercury in fish tissue and dissolved methylmercury in the water column, data can be collected to determine the relationship between methylmercury in fish tissue and total recoverable methylmercury or dissolved or total recoverable mercury in the water column. The Great Lakes Water Quality Initiative (GLI) used site-specific BAFs to convert directly from methylmercury in fish to total recoverable mercury in the water column. See 40 CFR part 132, and appendix B to part 132, Methodology for Deriving Bioaccumulation Factors.

bioaccumulation are incorporated within the measurements used to derive the BAF. Specifically, it is not required that the exact relationship between methylmercury accumulation and the factors that can influence it be understood or quantified to derive a site-specific BAF. By measuring the methylmercury concentrations empirically, these factors have been incorporated such that site-specific BAFs provide an accounting of the uptake and accumulation of methylmercury for an organism in a specific location and at a specific point in time.

Limitations to the site-specific BAF approach relate primarily to its cost and empirical nature. For example, the level of effort and associated costs of developing site-specific BAFs increase as the spatial scale of the site of interest increases. Furthermore, the amount of data necessary to obtain a representative characterization of methylmercury in the water and fish might take considerable time to gather. (For a discussion on sampling considerations for developing a site-specific BAF, see section 3.1.3.2.) The strictly empirical nature of this approach is also a barrier to extrapolating BAFs among species, across space, and over time because the site-specific factors that might influence bioaccumulation are integrated within the tissue concentration measurement and thus cannot be individually adjusted to extrapolate to other conditions.

3.1.3.1.2 Bioaccumulation models

Bioaccumulation models for mercury vary in the technical foundation on which they are based (empirically or mechanistically based), spatial scale of application (specific to waterbodies, watersheds or regions, and species of fish), and level of detail in which they represent critical bioaccumulation processes (simple, mid-level, or highly detailed representations). Thus, it is critical that states and tribes use a model that is appropriately developed, validated, and calibrated for the species and sites of concern.

Empirical bioaccumulation models that explicitly incorporate organism-, water-chemistry-, and waterbody/watershed-specific factors that might affect methylmercury bioaccumulation (e.g., fish species, age, length, pH, DOC, sulfate, alkalinity, sediment acid-volatile sulfide concentration, proximity to wetlands, land use, morphology, hydrology, productivity) usually take the form of multivariate regression models. Many examples of such models are available in the literature (e.g., Brumbaugh et al. 2001; Kamman et al. 2004; Sorensen et al. 1990). The model developed by Brumbaugh et al. (2001) is based on a national pilot study of mercury in 20 watersheds throughout the United States. Specifically, Brumbaugh et al. (2001) developed a multiple regression relationship between five factors: length-normalized mercury concentration in fish, methylmercury concentration in water, percentage of wetland area in the watershed, pH, and acid-volatile sulfide concentration in sediments ($r^2 = 0.45$; all fish species). When data were restricted to a single species (e.g., largemouth bass) and a single explanatory variable (e.g., methylmercury in water), a highly significant relationship was found ($p < 0.001$) with a similar degree of correlation ($r^2 = 0.50$). This demonstrates the importance of species specificity in the strength of such regression relationships and, in this case, methylmercury in water as an explanatory variable.

States and tribes should consider several important issues when using regression-based bioaccumulation models for translating from a tissue concentration to a water column concentration. First, a number of such regression models have been developed without

explicitly incorporating methylmercury (or mercury) concentrations in the water column. Instead, the models relate fish tissue methylmercury concentrations to variables that serve as proxies for methylmercury exposure (e.g., atmospheric deposition rates, ratio of the watershed drainage to the wetland area, pH, lake trophic status), often because of the costs associated with obtaining accurate measurements of mercury in the water column. Obviously, such models cannot be directly solved for the parameter of interest (methylmercury in water). Second, correlation among independent or explanatory variables in these multiple regressions is common and expected (e.g., pH and methylmercury concentration in water). Such correlations among explanatory variables can cause bias and erroneous estimates of an explanatory variable (in this case, methylmercury concentration in water) when back-calculated from the regression equation (Neter et al. 1996). In such cases, using the underlying data set to develop a separate regression model with methylmercury concentration in water as the dependent variable is more appropriate. Last, because these regression models are based on empirical data, uncertainty is introduced when the results are extrapolated to aquatic ecosystems with different conditions. Only in a few cases have such models been tested using independent data sets (e.g., Kamman et al. 2004).

Mechanistic bioaccumulation models are mathematical representations of the natural processes that influence methylmercury bioaccumulation. The process of methylation itself is incompletely understood, and general models for reliably predicting rates of methylation do not exist, although EPA's WASP model might be useful in some environments. Three examples of mechanistic bioaccumulation models are the Dynamic Mercury Cycling Model, or D-MCM (EPRI 2002); the Bioaccumulation and Aquatic System Simulator, or BASS (Barber 2002), and the Quantitative Environmental Analysis Food Chain model, or QEAFDCHN (QEA 2000). A conceptual advantage of mechanistically based bioaccumulation models is that methylmercury bioaccumulation can be predicted under different conditions (e.g., different growth rates of fish, different water chemistry conditions, and different mercury loading scenarios) because the models include mathematical representations of various processes that affect bioaccumulation. This advantage comes at the cost of additional input data necessary to run the model. Notably, only a few models have been used to predict methylmercury bioaccumulation. Such models have not been widely used and have been applied only to mercury in a few aquatic ecosystems under specific environmental conditions. Of the examples listed above, only the D-MCM was developed specifically for mercury. The D-MCM has not been applied to lotic systems (i.e. streams, rivers, estuaries) and therefore probably should be used only for static environments (lakes) at this time. The other models have been developed more generally, for nonionic organic chemicals that bioaccumulate, and require substantial modification and validation for application to mercury.

Most mechanistic bioaccumulation models use a chemical mass balance approach to calculate bioaccumulation in fish or other aquatic organisms. This approach requires considerable understanding of mercury loadings to and cycling within the environment. None of the example models presented can predict bioaccumulation without considerable site-specific information, at least some degree of calibration to the waterbody of interest, and, in some cases, considerable modification of the model. The amount and quality of data necessary for proper model application may equal or exceed that necessary to develop site-specific methylmercury BAFs, although these models might also help in

determining BAFs if the kinetic condition in the waterbody is not steady state. Because of the need for site-specific data and calibration, these models are likely to cost as much to implement as a site-specific BAF. Their value comes from the ability to represent a wider range of explanatory and policy-relevant variables.

Regardless of the type of model used, states' and authorized tribes' methodologies should be consistent with the *Methodology for Deriving Ambient Water Quality Criteria for the Protection of Human Health* (section 5.6: National Bioaccumulation Factors for Inorganic and Organometallic Chemicals; USEPA 2000b) and *Technical Support Document Volume 2: Derivation of National Bioaccumulation Factors* (USEPA 2003). These documents provide detailed discussion of topics such as BAF derivation procedures, bioavailability, and the steps involved in procedures 5 and 6 of the Human Health Methodology. States and tribes should document how they derive the site-specific parameters used in the bioaccumulation models and should describe the uncertainty associated with the BAFs derived using any of the models.

3.1.3.1.3 Draft national bioaccumulation factors

EPA acknowledges that using site-specific BAFs or model-derived BAFs might not be feasible in all situations. Without site-specific methylmercury bioaccumulation data or an appropriate bioaccumulation model, another approach is to use EPA's empirically derived draft national methylmercury BAFs as defaults. EPA used *Technical Support Document Volume 3: Development of Site-Specific Bioaccumulation Factors* of the 2000 Human Health Methodology (USEPA 2000b, 2003) and the BAF methods in volume III, appendix D, of the *Mercury Study Report to Congress* (USEPA 1997c) to derive draft methylmercury BAFs as part of its initial efforts to derive a water column-based recommended section 304(a) ambient water quality criterion for methylmercury. These draft national BAFs were developed from field data collected from across the United States and reported in the published literature. The draft national BAFs and the uncertainties associated with them are discussed in appendix A, section I, of *Water Quality Criterion for the Protection of Human Health: Methylmercury* (USEPA 2001a). The draft national BAFs (50th percentile values) are listed by trophic level in table 2.

Table 2. Draft national BAFs for dissolved methylmercury

BAF trophic level 2 (L/kg)	BAF trophic level 3 (L/kg)	BAF trophic level 4 (L/kg)
120,000	680,000	2,700,000

Source: USEPA 2001a.

Note: Expressed as milligrams methylmercury/kilogram fish tissue per milligram methylmercury/liter water, or liters per kilogram (L/kg).

To develop the draft national BAFs for each trophic level, EPA calculated the geometric mean of the field-measured BAFs obtained from the published literature. EPA believes the geometric mean BAFs are the best available central tendency estimates of the magnitude of BAFs nationally, understanding that the environmental and biological conditions of the waters of the United States are highly variable. Specifically, the data presented in *Water Quality Criterion of the Protection of Human Health: Methylmercury* (USEPA 2001a) indicate that BAFs for trophic levels 3 and 4 vary by a factor of 100

(two orders of magnitude) between the 5th and 95th percentiles. EPA does not recommend basing an AWQC on BAF values associated with the extremes of the distribution (e.g., 10th or 90th percentile), unless supported by site-specific data. Such values might introduce an unacceptable level of uncertainty into the calculation of a water column-based AWQC. States and authorized tribes should consider the magnitude of the potential error when proposing to use the draft national BAFs.

When states and authorized tribes calculate a water column-based criterion using draft national BAFs that differ greatly from the BAFs for the waterbody of concern, the resulting water column-based criterion will be either over- or under-protective. As a result, evaluation of the results of the analysis of water samples might result in the false conclusion that a fish tissue concentration has been exceeded (when it actually has not) or a false conclusion that a fish tissue concentration has not been exceeded (when it actually has). For more information on the draft national BAFs, see chapter 6 and appendix A, section I, of EPA's 304(a) water quality criterion for methylmercury (USEPA 2001a). The following examples illustrate the potential impact of calculating a water quality criterion using a BAF that is substantially different from the actual BAF.

- *Underprotective scenario*
  A state uses the draft national BAF of 2,700,000 L/kg for trophic level 4 fish, but the BAF based on site-specific data for the trophic level 4 fish in the waterbody is three times that, or 8,100,000 L/kg. In using the draft national BAF, a state would consider water column concentrations up to 0.11 nanogram per liter (ng/L) (0.3 mg/kg / 2,700,000 L/kg) to indicate attainment of the water quality column criterion. Using the BAF based on site-specific data, however, a water column criterion of 0.11 ng/L would correspond to a fish tissue concentration of 0.9 mg/kg, which is three times the 0.3 mg/kg criterion recommended to protect human health. Thus, load reductions or permits using the draft national BAF of 2,700,000 L/kg would be underprotective.

- *Overprotective scenario*
  A state uses the draft national BAF of 2,700,000 L/kg for trophic level 4 fish, but the BAF based on site-specific data for the trophic level 4 fish in the waterbody is one-third that, or 900,000 L/kg. As a result, a state would consider water column concentrations up to 0.11 ng/L (0.3 mg/kg / 2,700,000 L/kg) to indicate attainment of the water quality criterion. Using the BAF based on site-specific data, however, attainment of the water quality criterion could be achieved at a higher water column concentration, 0.33 ng/L. Thus, load reductions or permits using the draft national BAF of 2,700,000 L/kg would be overprotective.

EPA cautions water quality managers that methylmercury bioaccumulation is generally viewed as a site-specific process and that BAFs can vary greatly across ecosystems. The uncertainty in the estimates of a draft national BAF comes from uncertainty arising from natural variability, such as size of individual fish, and from uncertainty due to measurement error, such as error in measurements of mercury in water or lack of knowledge of the true variance of a process (e.g., methylation). Users of the draft national BAFs are encouraged to review appendix A of *Water Quality Criterion for the Protection of Human Health: Methylmercury* (USEPA 2001a), which describes the uncertainties

inherent in these values. The following is a synopsis of the discussion of uncertainty in that appendix.

- *Uncertainty due to sampling and chemical analysis:* In many cases, water methylmercury concentrations reported in the available studies incorporated limited or no cross-seasonal variability, incorporated little or no spatial variability, and were often based on a single sampling event. Because fish integrate exposure of mercury over a lifetime, comparing fish concentrations to a single sample or mean annual concentrations introduces bias to the estimates. The geographic range represented by the waterbodies was also limited.

- *Uncertainty due to estimation method:* The approaches used to estimate the draft national BAFs have their own inherent uncertainties. The approaches assume that the underlying process and mechanisms of mercury bioaccumulation are the same for all species in a given trophic level and for all waterbodies. They are also based on a limited set of data.

- *Uncertainty due to biological factors:* With the exception of deriving BAFs on the basis of river or lake waterbody type, there were no distinctions in the BAFs as to the size or age of fish, waterbody trophic status, or underlying mercury uptake processes. In reality, methylmercury bioaccumulation for a given species can vary as a function of the age (body size) of the organisms examined.

- *Uncertainty due to universal application of BAFs:* There is uncertainty introduced by failure of a single trophic-level-specific BAF to represent significant real-world processes that vary from waterbody to waterbody. The simple linear BAF model relating methylmercury in fish to mercury in water simplifies a number of nonlinear processes that lead to the formation of bioavailable methylmercury in the water column and subsequent accumulation. Much of the variability in field data applicable to the estimation of mercury BAFs can be attributed to differences in biotic factors (e.g., food chain, organism age or size, primary production, methylation or demethylation rates) and abiotic factors (e.g., pH, organic matter, mercury loadings, nutrients, watershed type or size) between aquatic systems. Unfortunately, although the concentration of methylmercury in fish tissue is presumably a function of these varying concentrations, published BAFs are typically estimated from a small number of measured water values whose representativeness of long-term exposure is not completely understood. Furthermore, although it is known that biotic and abiotic factors control mercury exposure and bioaccumulation, the processes are not well understood, and the science is not yet available to accurately model bioaccumulation on a broad scale.

Peer reviewers expressed concerns about the use of the draft national BAFs as defaults to predict bioaccumulation across all ecosystems and about using them to derive a national recommended section 304(a) water quality criterion for methylmercury that would suitably apply to waterbodies across the nation. EPA recognized the peer reviewers' concerns and acknowledges that these draft national BAF values might significantly over- or underestimate site-specific bioaccumulation. As a result, EPA decided not to use the draft national BAFs to develop a national water-column-based AWQC for methylmercury. Furthermore, the draft national BAFs are EPA's least preferred means

for assessing the BAF. States and tribes should also consider whether more recent data and/or data that are more reflective of local conditions are available to supplant or supplement the limited database used to derive the draft national BAFs.

Risk managers should also understand that in using the draft national BAFs as defaults, one assumes that the biotic and abiotic processes affecting mercury fate and bioaccumulation are similar across different waterbodies, and therefore using the draft national BAFs does not address site-specific factors that might increase or decrease methylation and bioaccumulation. A state's or tribe's decision to use the draft national BAFs would be a risk management decision. The decision would reflect the state's or tribe's judgment that, for specific reasons, translating the fish tissue criterion to a water column value using such a BAF is preferable to implementing the fish tissue criterion directly (e.g., using the approaches discussed in this guidance), or conducting studies to develop a site-specific BAF (e.g., site-specific field studies or bioaccumulation modeling).

3.1.3.2 What are the sampling considerations for deriving site-specific field-measured BAFs?

For both fish tissue and water, states and authorized tribes should analyze for methylmercury when deriving site-specific BAFs. EPA has not yet published analytical methods to measure methylmercury in water or fish in 40 CFR part 136. A discussion of analytical methods for mercury and methylmercury can be found in section 4.1. For fish tissue, however, states and authorized tribes can estimate methylmercury concentrations and determine attainment by using the same analytical method used to measure for mercury, at least for upper-trophic-level fish (levels 3 and 4). This is because 80 to 100 percent of the mercury found in the edible portions of freshwater fish greater than three years of age from these two trophic levels is in the form of methylmercury (USEPA 2000c). In fish greater than approximately three years of age, mercury has had sufficient time to bioaccumulate to roughly steady levels in the fish. Appendix A summarizes eight studies of the relative proportion of the mercury concentration in North American freshwater fish that is in the form of methylmercury. In six of the eight studies, methylmercury on average accounted for more than 90 percent of the mercury concentration in fish tissue. In the remaining two studies, methylmercury on average accounted for 80 to 90 percent of the mercury concentration in trophic level 3 and 4 fish.

States and tribes should consider a number of issues when sampling aquatic organism tissue and water to derive a site-specific BAF. The goal of deriving site-specific methylmercury BAFs is to reflect or approximate the long-term bioaccumulation of methylmercury in commonly consumed aquatic organisms of a specified trophic level. Hence, an important sample design consideration is how to obtain samples of tissue and water that represent long-term, average accumulation of methylmercury. Methylmercury is often slowly eliminated from fish tissue. Therefore, concentrations of methylmercury in fish tissue tend to fluctuate much less than the concentration of methylmercury in water. Thus, for calculating representative site-specific BAFs, states and tribes should consider how to integrate spatial and temporal variability in methylmercury concentrations in both water and tissue. States and tribes should address the variability in methylmercury concentrations in fish tissue with age or size of the organism either by restricting sample collection to organisms of similar age or size classes or by using

appropriate normalization techniques. EPA's fish sampling guidance recommends that fish should be of similar size so that the smallest individual in a composite is no less than 75 percent of the total length (size) of the largest individual (USEPA 2000c). One way of normalizing data is by using the National Descriptive Model for Mercury in Fish Tissue, or NDMMF (Wente 2004). The NDMMF is a statistical model that normalizes Hg fish tissue concentration data to control for species, size, and sample type variability. An example use of the NDMMF is in the combination of mercury fish tissue data from two databases (USEPA 2005a).

States and tribes should assess the fish consumption patterns of the exposed human population when designing a site-specific sampling plan. Because the age and size of aquatic organisms are correlated with the magnitude of methylmercury accumulation, the types and sizes of aquatic organisms being consumed should be considered when determining which fish to sample for deriving BAFs. States and tribes should consider the fish being consumed by various subpopulations (e.g., sport anglers, subsistence fishers) as well as culturally and economically diverse communities. This information should also guide the decision on whether the site-specific BAF should be based on a single trophic level (e.g., trophic level 4) or on multiple trophic levels.

States and authorized tribes should review site-specific data used to calculate field-measured BAFs and thoroughly assess the quality of the data and the overall uncertainty in the BAF values. States and authorized tribes should also consider the following general factors when determining the acceptability of field-measured BAFs reported in the published scientific literature. The same general issues and questions should also be addressed when designing a field study to generate site-specific field-measured BAFs.

- Calculate a field-measured BAF using aquatic organisms that are representative of the aquatic organisms commonly consumed at the site of interest (e.g., river, lake, ecoregion, state). Review information on the ecology, physiology, and biology of the target organisms when assessing whether an organism is a reasonable surrogate of a commonly consumed organism.

- Determine the trophic level of the study organism by taking into account its life stage, its diet, and the food web structure at the study location. Information from the study site (or similar sites) is preferred when evaluating trophic status. If such information is lacking, states and authorized tribes can find general information for assessing the trophic status of aquatic organisms in *Guidance for Assessing Chemical Contaminant Data for Use in Fish Advisories*, volume 1, *Fish Sampling and Analysis* (USEPA 2000c).

- Collect length, weight, and age data for any fish used in deriving a field-measured BAF because current information suggests that variability in methylmercury accumulation is dependent on fish age and size (USEPA 2001a). This information helps normalize the BAF to a standardized fish size within the range of fish sizes and species known to be consumed by the human population of interest.

- Verify that the study used to derive the field-measured BAF contains sufficient supporting information from which to determine that tissue and water samples were collected and analyzed using appropriate, sensitive, accurate, and precise analytical methods.

- Verify that the water concentrations used to derive a BAF reflect the average exposure of the aquatic organism of concern that resulted in the concentration measured in its tissue. Concentrations of methylmercury in a waterbody vary seasonally and diurnally (Cleckner et al. 1995) because of a variety of biological and physical factors.

- Attempt to design a field sampling program that addresses potential temporal and spatial variability and that allows estimation of average exposure conditions. The study should be designed to sample an area large enough to capture the more mobile organisms and also to sample across seasons or multiple years when methylmercury concentrations in waters are expected to have large fluctuations. Longer sampling durations are necessary for waters experiencing reductions in mercury loadings, changes in water chemistry that affect methylation, and changes in the composition of the food web.

Volume I of the *Guidance for Assessing Chemical Contaminant Data for Use in Fish Advisories* (USEPA 2000c) provides additional guidance on selecting target species to sample, specific sampling design procedures, analytical measurement procedures, and quality assurance guidance. Chapter 10 of EPA's *Exposure Factors Handbook* provides additional guidance on collecting information about local species (USEPA 1997d). Additional guidance on evaluating existing site-specific bioaccumulation studies for use in deriving trophic-level-specific BAFs and designing sampling plans for obtaining data for deriving site-specific BAFs is provided in *Technical Support Document—Volume 2: Developing National Bioaccumulation Factors* (USEPA 2003). A publication by Burkhard (2003) is also a good source of information on designing BAF field studies and on deriving field-measured site-specific BAFs.

3.1.3.3 How is methylmercury in water translated into its mercury equivalent in water?

Given that permit limits are often derived using a mercury water column concentration criterion, a state or tribe may wish to take another step after using a BAF to determine a methylmercury water concentration criterion to derive a mercury water column concentration criterion. Although not necessary to develop a water quality criterion, a state can translate a methylmercury water concentration into a mercury water concentration criterion by converting the concentration of methylmercury in water to the equivalent concentration of mercury in water. This step might be necessary because although the BAF is typically based on the concentration of methylmercury in water, the assessment of water quality is typically based on an evaluation of mercury concentrations since other forms of mercury are converted to methylmercury in the environment. As a result, a relationship between (dissolved or total recoverable) methylmercury and (dissolved or total recoverable) mercury in the water needs to be developed. NPDES permits and other water quality-based pollution control activities traditionally rely on the total recoverable concentration of mercury, not the dissolved methylmercury form.

Many of the issues surrounding the uncertainty in predicting and transferring methylmercury BAFs across different waterbodies also apply to translating methylmercury concentrations to mercury concentrations. As with BAFs, one approach for translating between methylmercury and mercury concentrations is for states and

authorized tribes to measure site-specific concentrations of methylmercury and mercury to determine the relative amounts of each form. This field-measured, site-specific approach is the most direct and the most appropriate approach to the translation.

Where a site-specific approach is not feasible, states and authorized tribes may consider applying EPA's draft national methylmercury-to-mercury translator factors. In the 2001 methylmercury criterion document (USEPA 2001c), EPA derived these translator factors for rivers/streams and lakes as geometric means from data collected from the literature reporting concentrations of mercury in aquatic environments. Thus, like the draft national BAFs, the methylmercury-to-mercury translators were empirically derived based on various water data from across the United States. As with the draft national BAFs, the draft national methylmercury-to-mercury translator factors vary greatly across ecosystems and are subject to many of the same uncertainties. Therefore, EPA suggests that states and tribes that may be considering using the draft national translator values as defaults carefully review the discussion in the 2001 criterion document, particularly the discussions concerning uncertainty and limitations, before deciding to apply them in a regulatory context (see appendix A, section II, USEPA 2001a). States and tribes should consider whether more recent data and/or data that are more reflective of local conditions are available to supplant or supplement the limited database used to derive the draft national translators.

Alternatively, states and tribes that choose to develop water column criteria can consider collecting data to develop BAFs that relate methylmercury in fish tissue directly to total mercury in the water column. See the footnote to section 3.1.3.1.1 for more information.

3.2 What options are available to address site-specific conditions and concerns?

3.2.1 How can the methylmercury water quality criterion be modified for site-specific conditions?

The 2000 Human Health Methodology (USEPA 2000b) describes how states and authorized tribes can adopt site-specific modifications of a section 304(a) criterion to reflect local environmental conditions and human exposure patterns. "Local" may refer to any appropriate geographic area where common aquatic environmental or exposure patterns exist. Thus, it may signify a statewide or regional area, a river reach, or an entire river. Such site-specific criteria may be developed as long as the site-specific data, either toxicological or exposure-related, are justifiable. For example, when using a site-specific fish consumption rate, a state or authorized tribe should use a value that represents at least the central tendency for the consumption rate of the population surveyed. When defining a target population, a state or authorized tribe should focus on protecting populations with high rates of fish consumption from the local area.

States and authorized tribes may modify EPA's recommended 304(a) criterion for methylmercury by using different assumptions for certain components of EPA's criterion to derive a criterion that maintains and protects the designated uses. For example, states and authorized tribes may:

- Use an alternative RSC factor or

- Use a daily uncooked freshwater and estuarine fish consumption rate that is more reflective of local or regional consumption patterns than the 17.5 grams/day default value. EPA encourages states and authorized tribes to consider using local or regional consumption rates instead of the default values if the former would better reflect the target population.

If a state or authorized tribe intends to modify both the RSC and the fish consumption rate, it might find collecting the data at the same time advantageous.

3.2.1.1 How does one modify the RSC?

Section 5 of the methylmercury criterion document (USEPA 2001a) provides detailed discussions on how EPA assessed exposure to methylmercury and how EPA derived the RSC factor used in calculating the criterion. The methylmercury RSC is an exposure, subtracted from the RfD to account for exposure to methylmercury from sources other than freshwater or estuarine fish. By accounting for other known exposures, the RSC seeks to ensure that methylmercury exposures do not exceed the RfD.

If a state or tribe proposes to change the RSC, it should document the modifications with data supporting the modifications and share the proposed modifications to the RSC with EPA prior to recalculating the criterion. See appendix B for the tables from the methylmercury criterion document. States and authorized tribes should review section 5 of the methylmercury criterion document and modify the media-specific exposure estimates using local data that reflect the exposure patterns of their populationsTo modify this factor, states and authorized tribes should review the amount of marine fish and shellfish estimated to be consumed (table 5-1, USEPA 2001a) and the concentration of methylmercury in the commonly consumed marine species (table 5-14, USEPA 2001a).

3.2.1.2 How does one modify the daily fish intake rate?

EPA derived the recommended methylmercury water quality criterion on the basis of a default fish intake rate for the general population (consumers and nonconsumers) of 17.5 grams/day[12], uncooked (USEPA 2001a). States and authorized tribes may use a different intake rate based on local or regional consumption patterns and are encouraged to use consumption rates that are protective of a range of culturally and economically diverse communities. The fish consumption value in the TRC equation may be changed if the target population eats a higher or lower amount of fish. For example, if the 90th percentile of a target population eats approximately 15 grams/day of freshwater and estuarine fish of various trophic levels, the fish intake value in equation 1 would simply be 15 grams/day, rather than the national default value of 17.5 grams/day used in calculating the 0.3 mg/kg TRC.

EPA encourages states and authorized tribes to develop a water quality criterion for methylmercury using local or regional fish consumption data rather than the default values if they believe that such a water quality criterion would be more appropriate for

[12] This value represents the 90th percentile of freshwater and estuarine finfish and shellfish consumption reported by the 1994–1996 *Continuing Survey of Food Intakes by Individuals*. For more information, see *Methodology for Deriving Ambient Water Quality Criteria for the Protection of Human Health* (USEPA 2000b).

their target population. However, states and authorized tribes should consider whether the fish consumption rates reflect existing public concern about contamination of fish when collecting survey data, rather than local preference for fish consumption (i.e., the presence of fish advisories limits the consumption of fish). In this instance, the state or authorized tribe should take this into account and try to conduct surveys in a manner that accounts for the effects of fish advisories on the consumption of fish. Where there is afish consumption advisory, surveys should be designed to evaluate how much fish a local population would consume if the fish were safe to eat and incorporate that consumption level into the criterion.

EPA suggests that states and authorized tribes follow a hierarchy when deriving fish intake estimates (USEPA 2000b). From highest preferred to lowest preferred, this hierarchy is as follows (1) use local data protective of culturally and economically diverse communities when available, (2) use data reflecting similar geography or population groups, (3) use data from national surveys, and (4) use EPA's default fish intake rates. Additional discussion of these four preferences is provided below.

When a state or authorized tribe develops a site-specific criterion on the basis of local fish consumption, site-specific BAFs, or a site-specific RSC, states and authorized tribes might want to include EPA in the development of the study plan and submit the data supporting the site-specific criterion for EPA's consideration when EPA approves or disapproves state or tribal water quality standards under CWA section 303(c). Including EPA at the study plan development stage may help to avoid problems and facilitate development of a defensible site-specific criterion.

3.2.1.2.1 Use local data

If a state or authorized tribe believes a fish consumption rate other than the default would be appropriate for their target population, EPA's first preference is that they use fish intake rates derived from studies of consumption of local fish. Such studies could include results of surveys designed to obtain information on the consumption of freshwater or estuarine species caught from local watersheds within the state or tribal jurisdiction. When estimating the fish intake rate, all freshwater fish, whether caught recreationally or bought commercially, should be included. States and authorized tribes may choose to develop either fish intake rates for the local population as a whole, or individual fish intake rates for various subpopulations (e.g., sport anglers, subsistence fishers) as well as culturally and economically diverse consumers.

States and authorized tribes might wish to conduct their own surveys of fish intake. *Guidance for Conducting Fish and Wildlife Consumption Surveys* (USEPA 1998a) provides EPA guidance on methods for conducting such studies. States and authorized tribes should take care to ensure that the local data are of sufficient quality and scope to support development of a criterion and are representative of the population of people that eat local fish. EPA's consumption survey guidance offers recommendations on how to develop appropriate quality assurance and quality control procedures to help ensure the quality of the survey. Results of studies of the broader geographic region in which the state or authorized tribe is located can also be used, but they might not be as applicable as study results for local watersheds. Because such studies would ultimately form the basis of a state's or authorized tribe's methylmercury criterion, EPA would consider any surveys of

fish intake as part of its review of the methylmercury criterion's scientific defensibility as part of the Agency's review of water quality standards under CWA section 303(c).

States and authorized tribes may use either high-end (such as 90th or 95th percentile) or central tendency (such as median or mean) consumption values for the population of interest (e.g., subsistence fishers, sport fishers, or the general population). EPA generally recommends that a central tendency value be the lowest value states or authorized tribes should use when deriving a criterion. When considering median values from fish consumption studies, states and tribes should ensure that the distribution is based on survey respondents that reported consuming fish because surveys of both consumers and nonconsumers can often result in median values of zero. EPA believes the approach described above is a reasonable procedure and is also consistent with other Agency positions such as that of the Great Lakes Water Quality Initiative, known as the GLI (USEPA 1995a).

3.2.1.2.2 Use similar geography or population groups

If surveys conducted in the geographic area of the state or authorized tribe are not available, EPA's second preference is that states and authorized tribes consider results from existing surveys of fish intake in similar geographic areas and population groups (e.g., from a neighboring state or authorized tribe or a similar watershed type) and follow the method described above regarding target values to derive a fish intake rate. For instance, states or tribes with subsistence fisher populations might wish to use consumption rates from studies that focus specifically on these groups, or use rates that represent high-end values from studies that measured consumption rates for a range of types of fishers (e.g., recreational or sport fishers, subsistence fishers, minority populations). A state or authorized tribe in a region of the country might consider using rates from studies that surveyed the same region; for example, a state or authorized tribe that has a climate that allows year-round fishing might underestimate consumption if it uses rates from studies taken in regions where people fish for only one or two seasons per year. A state or authorized tribe that has a high percentage of an age group (such as older persons, who have been shown to have higher rates in certain surveys) might wish to use age-specific consumption rates, which are available from some surveys. For additional information on the use of fish consumption rates, see EPA's 2000 Human Health Methodology (USEPA 2000b). Again, EPA recommends that states and tribes use only uncooked weight intake values and freshwater or estuarine species data.

3.2.1.2.3 Use national surveys

If applicable consumption rates are not available from local, state, or regional surveys, EPA's third preference is that states and authorized tribes select intake rate assumptions for different population groups from national food consumption surveys. EPA has analyzed two such national surveys, the 1994–1996 and 1998 Continuing Survey of Food Intakes by Individuals (CSFII). These surveys, conducted by the U.S. Department of Agriculture (USDA), include food consumption information from a probability sample of the population of all 50 states. Respondents to the survey provided 2 days of dietary recall data. A separate EPA report provides a detailed description of the combined 1994–1996 and 1998 CSFII surveys, the statistical methodology, and the results and uncertainties of the EPA analyses (USEPA 2002b). The estimated fish consumption rates

in the CSFII report are presented by fish habitat (i.e., freshwater or estuarine, marine, and all habitats) for the following population groups: (1) all individuals, (2) individuals age 18 and over, (3) women ages 15–44, and (4) children age 14 and under. Three kinds of estimated fish consumption rates are provided: (1) per capita rates (rates based on consumers and nonconsumers of fish from the survey period), (2) by consumers-only rates (rates based on respondents that reported consuming finfish or shellfish during the 2-day reporting period), and (3) per capita consumption by body weight (per capita rates reported as mg/kg-day). For purposes of revising the fish consumption rate in the methylmercury criterion, EPA recommends using the rates for freshwater and estuarine fish and shellfish.

The CSFII surveys (USDA/ARS 1998, 2000) have advantages and limitations for estimating per capita fish consumption. The primary advantage of the CSFII surveys is that USDA designed and conducted them to support unbiased estimation of food consumption across the population in the United States and the District of Columbia. One limitation of the CSFII surveys is that individual food consumption data were collected for only 2 days—a brief period that does not necessarily depict "usual intake." Usual dietary intake is defined as "the long-run average of daily intakes by an individual." Upper percentile estimates might differ for short-term and long-term data because short-term food consumption data tend to be inherently more variable. It is important to note, however, that variability due to duration of the survey does not result in bias of estimates of overall mean consumption levels. Also, the multistage survey design does not support interval estimates for many of the subpopulations because of sparse representation in the sample. Subpopulations with sparse representation include American Indians on reservations and certain ethnic groups. Although these persons were participants in the survey, they were not present in sufficient numbers to support fish consumption estimates. The survey does support interval estimates for the U.S. population and some large subpopulations (USEPA 2002b).

3.2.1.2.4 Use EPA default fish intake rates

EPA's fourth preference is that states and authorized tribes use as fish intake assumptions, default rates on the basis of the 1994–1996 CSFII data for the U.S. population, which EPA believes are representative of freshwater and estuarine fish and shellfish intake for different population groups. The 1994–1996 CSFII data for U.S. fish consumption among both consumers and nonconsumers of fish is delineated below in table 3.

Because the combined 1994–1996 CSFII survey is national in scope, EPA uses the results from it to estimate fish intake for deriving national criteria. EPA applies a default rate of 17.5 grams/day for the general adult population. EPA selected an intake rate that is protective of a majority of the population (the 90th percentile of consumers and nonconsumers, according to the 1994–1996 CSFII survey data) (USEPA 2000b). EPA also recommends a default rate of an average of 17.5 grams/day for sport fishers.

Table 3. Estimates of freshwater and estuarine combined finfish and shellfish consumption from the combined 1994–1996 and 1998 CSFII surveys (U.S. population)

	Mean	Median	90th percentile	95th percentile	99th percentile
All ages	6.30	N/a	11.65	41.08	123.94
Age 18 and over	7.50	0.00*	17.53	49.59	142.41
Women ages 15-44	5.78	N/a	6.31	32.37	109.79
Children age 14 and under	2.64	0.00	0.00	13.10	73.70

Note: All values expressed as grams per day for uncooked fish.

* The median value of 0 grams/day might reflect the portion of persons in the population that never eat fish, as well as the limited reporting period (2 days) during which intake was measured.

Similarly, EPA believes the 99th percentile of 142.4 grams/day is within the range of consumption estimates for subsistence fishers, according to the studies reviewed, and that it represents an average rate for subsistence fishers. EPA knows that some local and regional studies indicate greater consumption among American Indian, Pacific Asian American, and other subsistence consumers and recommends the use of those studies in appropriate cases, as indicated by the first and second preferences. Again, states and authorized tribes have the flexibility to choose intake rates higher than the average values for these population groups. If a state or authorized tribe has not identified a separate well-defined population of exposed consumers and believes that the national data from the 1994–1996 CSFII are representative, the state or tribe may choose these recommended rates.

EPA has made these risk management decisions after evaluating numerous fish intake surveys. These values represent the uncooked weight intake of freshwater and estuarine finfish and shellfish. As with the other preferences, EPA requests that states and authorized tribes routinely consider whether a substantial population of sport fishers or subsistence fishers exists in the area when establishing water quality criteria rather than automatically using data for the general population.

The CSFII surveys also provide data on marine species, but EPA considered only freshwater and estuarine fish intake values for determining default fish consumption rates because EPA considered exposure from marine species of fish in calculating an RSC for dietary intake.[13] States and authorized tribes should ensure that when evaluating overall exposure to a contaminant, marine fish intake is not double-counted with the other dietary intake estimate used. Coastal states and authorized tribes that believe accounting for total fish consumption (fresh or estuarine *and* marine species) is more appropriate for protecting the population of concern may do so, provided that the marine intake component is not double-counted with the RSC estimate (USEPA 2000b).

[13] See the discussion of the RSC in sections 3.1.2.3 and 3.2.1.1.

3.2.2 How do water quality standards variances apply?

Where a discharger or waterbody cannot meet a water quality standard, a state or authorized tribe may adopt a temporary water quality standard through a variance process. The variance would then, in effect, serve as a substitute standard for a point source, and the WQBEL contained in an NPDES permit would then be based on the variance. As a revision to the otherwise applicable water quality standard (designated use and criteria), water quality standards variances must be supported by one of the six justifications under 40 CFR 131.10(g) (see section 3.2.3.4 below). Variances are generally determined based on the discharger's ability to meet a WQBEL and, therefore, are considered after an evaluation of controls necessary to implement water quality standards. In addition, EPA recommends that the permitting authority require the facility seeking a variance to develop and implement a mercury minimization plan (MMP) to both reduce mercury loading and to determine the highest level of water quality achievable to inform future permit decisions (see section 7.5.2.4 for more discussion of MMPs).

Variances typically apply for a limited period but may be reviewed at the time of the state triennial review of water quality standards, and require the same procedural steps that are required of a change in the standards. Where the term of a variance extends beyond three years, as for example in an NPDES permit, the variance must still be reassessed as part of the state's three year triennial review to confirm that the underlying attainability analysis remains relevant and accurate. A variance must continue to protect "existing uses" (defined in 40 CFR 131.3(e) as uses actually attained in the waterbody on or after November 28, 1975). Typically, variances apply to specific pollutants and facilities, which would mean that a water quality standards variance for mercury would apply to only the new methylmercury criterion in a stated waterbody and specifically to the discharger requesting the variance. The state or authorized tribe, however, may provide justification for more than one discharger or for an entire waterbody or segment to receive a variance (as discussed in section 3.2.2.3 of this document). See section 3.2.3 for a discussion of the requirement to conduct a use attainability analysis for changes to water quality standards, including the prohibition on removing existing uses.

3.2.2.1 When is a variance appropriate?

Some regulated point sources discharging mercury might apply for variances for their discharges into impaired waters where the largest source of mercury is atmospheric deposition. In other cases, limits to technology or naturally elevated levels of methylmercury in a waterbody could preclude attainment of standards. To address these types of issues, the following scenarios are examples of demonstrations that could satisfy the requirements under 40 CFR 131.10(g). The demonstrations are more thoroughly explained below and in the *Water Quality Standards Handbook* (USEPA 1994).

- *Economic or social impacts* (131.10(g)(6)). Demonstrate that, in the short term, the costs of constructing controls necessary to meet the methylmercury criterion (beyond those required by sections 301(b)(1)(A) and (B) and 306 of the CWA) would result in substantial and widespread economic and social impact.

- *Human-caused conditions that cannot be remedied* (131.10(g)(3)). Demonstrate that, in the short term, none of the present technologies for improving the quality of

an effluent are capable of bringing methylmercury levels in the discharge down to a level as stringent as necessary to meet the criterion (i.e., there is no technological remedy or it is technologically infeasible).

- *Natural conditions that preclude attainment* (131.10(g)(1)). Demonstrate that local conditions of an aquatic system result in high methylmercury levels. For example, elevated methylmercury concentrations might occur naturally in a system because of a short-term condition.

During the period the variance applies, any permit issued must be consistent with applicable water quality standards (40 CFR 122.44(d)(1)(vii)), which in this case would be the temporary standard approved in the variance. The permit would need to be modified to derive from and comply with the underlying standard if the variance is not re-issued.

3.2.2.2 What should a state or tribe consider before granting a variance?[14]

In general, the temporary revised standard established by a variance should be set at a level representing the highest attainable water quality (like all water quality standards). Variances may not interfere with existing uses, and variances should ensure progress toward ultimate attainment of the designated use for the waterbody. Regarding procedural considerations, the same requirements apply for a variance as for a new or revised standard (e.g., public review and comment, EPA approval or disapproval) because a variance is a change to the water quality standards. In addition, the following describes more specific issues that states and authorized tribes should take into account when considering granting a variance.

- *Variance protocols.* If a state or authorized tribe anticipates receiving a number of variance requests for mercury discharges, it could consider establishing a mercury variance protocol, with EPA's participation and agreement. The protocol would govern the development and processing of variance requests. It would specify the information needed and the criteria the state would use in considering whether to adopt the variance. Although the state or tribe would need to submit each variance to EPA for approval (40 CFR 131.20), EPA's advance agreement to the protocol could streamline EPA's review of any variances developed in accordance with the protocol. Public notice requirements for variances could be satisfied through the process of issuing the NPDES permit that incorporates limits based on such temporary standards, as long as the variance is identified and all the necessary information pertaining to the variance is included.

- *Time frames.* A variance is typically a time-limited change in the water quality standards. Although EPA part 131 regulations do not specify a time limit for variances, EPA's triennial review regulations at 40 CFR 131.20 require that variances, as part of water quality standards, are reexamined every three years to

[14] Federal or state regulations also govern the granting of a variance. For example, regulations promulgated under 40 CFR part 132, appendix F, procedure 2, specify the conditions for granting variances in the Great Lakes and prohibit the granting of variances to new dischargers or recommending Great Lakes dischargers.

determine if new information has become available and modified as appropriate. Variances that extend longer than three years are traditionally revisited in the context of a triennial review. Once a variance has expired, to justify the continuation of the variance, the state must demonstrate that meeting the standard is still unattainable based on one of the factors at 131.10(g). The state should also ensure that the permittee has made reasonable progress to control mercury in the discharge during the period of the previously approved variance (i.e. has adopted a mercury minimization plan.)

As with any other revision to the water quality standards, the permit and permit conditions implementing the variance do not automatically change back to the previous permit conditions if the variance expires, unless that is a condition of a variance and permit. Although water quality standards can change with every triennial review, states and authorized tribes are not obliged to reopen and modify permits immediately to reflect those changes, but may do so where the permit contains a reopener condition to address such revised water quality standards. In the Great Lakes, however, permits with limits based on variances must include a provision enabling the permitting authority to reopen and modify the permit based on triennial revisions to water quality standards. (40 CFR part 132, appendix F, procedure 2, section F.4). Any new or reissued permit must implement the water quality standards applicable at time of permit issuance. 40 CFR 122.44(d)(1).

- *Antidegradation.* Permits with effluent limits based on a variance for methylmercury must conform, as do all permits, to the state or authorized tribe's antidegradation policy.

- *Mercury Minimization Plans (MMPs).* EPA recommends that states and authorized tribes require dischargers receiving a variance to adopt and implement an MMP as described in section 7.5.2.4. By reducing mercury sources up front, as opposed to traditional reliance on treatment at the end of a pipe, diligent implementation of MMPs might mitigate any adverse effects of a variance by improving the water quality. As noted above, MMPs also serve to inform the evaluation of controls needed to grant a variance and to determine the highest attainable water quality

3.2.2.3 What is involved in granting a variance on a larger scale?

Traditionally, variances are specific to a pollutant and a facility. However, for situations where a number of NPDES dischargers are located in the same area or watershed and the circumstances for granting a variance are the same, states and authorized tribes may consider administering a multiple-discharger variance for a group of dischargers collectively. Such a group variance can be based on various scales and may depend largely on the rationale for adopting a variance for methylmercury. Possible applications of a group variance may include facilities with similar discharge processes, a watershed basis, particularly for states that issue NPDES permits on a watershed basis, or a broader geographic basis, analogous to a general NPDES permit.

For example, Ohio adopted a statewide mercury variance applicable to point source dischargers in the state that meet specified criteria. In addition, Michigan has authorized multiple discharger variances for mercury with permit requirements, including development and implementation of an MMP.

It is important to note that, despite the coverage of a multiple-source variance, an individual discharger must still demonstrate that the underlying criterion is not attainable with the technology-based controls identified by CWA sections 301(b) and 306 and with cost-effective and reasonable best management practices (BMPs) for nonpoint sources (40 CFR 131.10(h)(2)).

3.2.3 How are use attainability analyses conducted?

3.2.3.1 What is a use attainability analysis?

A use attainability analysis (UAA) is defined in 40 CFR 131.3(g) as a structured scientific assessment of the factors affecting the attainment of a use, which may include physical, chemical, biological, and economic factors, that must be conducted whenever a state wishes to remove a designated use specified in section 101(a)(2) of the CWA, or to adopt subcategories of uses specified in section 101(a)(2) of the CWA, which require less stringent criteria (see 40 CFR 131.3 and 40 CFR 131.10(g)).

Where a UAA indicates that the current use is unattainable, the state or tribe will need to identify and assign the "highest attainable use," which should reflect the factors and constraints on the attainability of a use that were evaluated as part of the UAA process. Once the state or tribe has determined the highest attainable use, it should propose adopting this designated use in place of the designated use deemed unattainable. For example, to the extent allowed by state or tribal law, the state or tribe could refine its designated use from "fish consumption" to "mercury-limited fish consumption." That way the waterbody would still be expected to meet other pollutant criteria designed to protect fish consumption.

3.2.3.2 What is EPA's interpretation of CWA section 101(a)?

CWA section 101(a) (2) establishes as a national goal "water quality [that] provides for the protection and propagation of fish, shellfish, and wildlife and provides for recreation in and on the water," wherever attainable. These goals are commonly referred to as the "fishable/swimmable" goals of the CWA. EPA interprets these goals as providing for the protection of aquatic communities and human health related to the consumption of fish and shellfish. In other words, EPA views "fishable" to mean that fish and shellfish can thrive in a waterbody and, when caught, can also be safely eaten by humans. This interpretation also satisfies the CWA section 303(c)(2)(A) requirement that water quality standards protect public health. Including human consumption of fish and shellfish as the appropriate interpretation of the definition of section 101(a)(2) uses is not new. For example, in the National Toxics Rule, all waters designated for even minimal aquatic life protection (and therefore a potential fish and shellfish consumption exposure route) are protected for human health (57 FR 60859, December 22, 1992).

3.2.3.3 When is a UAA needed for a "fishable" use?

Under 40 CFR 131.10(j) of the Water Quality Standards Regulation, states and authorized tribes are required to conduct a UAA whenever the state or authorized tribe designates or has designated uses that do not include the "fishable/swimmable" use specified in CWA section 101 (a)(2); or the state or authorized tribe wishes to remove a

designated use that is specified in CWA section 101(a)(2) or adopt subcategories of the uses specified in that section that require less stringent criteria.

An important caveat to the process of removing a designated use is that states and authorized tribes may not remove an "existing use" as defined by the Water Quality Standards Regulation. An existing use is defined in 40 CFR 131.3(c) as any use that has been actually attained on or after November 28, 1975, when the CWA regulations regarding use designation were originally established. In practical terms, waters widely used for recreational fishing would not be good candidates for removing a "fishable" use, especially if the associated water quality supports, or has until recently supported, the fishable use, on the basis, in part, of the "existing use" provisions of EPA's regulations.

In addition, EPA considers designated uses attainable, at a minimum, if the use can be achieved (1) through effluent limitations under CWA sections 301(b)(1)(A) and (B) and 306 and (2) through implementation of cost-effective and reasonable BMPs for nonpoint sources. The federal regulations at 40 CFR 131.10(g) further establish the basis for finding that attaining the designated use is not feasible, as long as the designated use is not an existing use. EPA emphasizes that when adopting uses and appropriate criteria, states and authorized tribes must ensure that such standards provide for the attainment and maintenance of the downstream uses (40 CFR part 131.10(b)). States and tribes are not required to conduct UAAs when designating uses that include those specified in CWA section 101(a) (2), although they may conduct these or similar analyses when determining the appropriate subcategories of uses.

3.2.3.4 What conditions justify changing a designated use?

EPA's regulations at 40 CFR 131.10(g) list the following six reasons for states or authorized tribes to use to support removal of a designated use or adoption of a subcategory of use that carries less stringent criteria:

- Naturally occurring pollutant concentrations prevent the attainment of the use.
- Natural, ephemeral, intermittent, or low-flow conditions or water levels prevent the attainment of the use, unless these conditions may be compensated for by the discharge of sufficient volume of effluent discharges without violating state water conservation requirements to enable uses to be met.
- Human-caused conditions or sources of pollution prevent the attainment of the use and cannot be remedied or would cause more environmental damage to correct than to leave in place.
- Dams, diversions, or other types of hydrologic modifications prevent the attainment of the use, and it is not feasible to restore the waterbody to its original condition or to operate such modification in a way that would result in attainment of the use.
- Physical conditions related to the natural features of the waterbody, such as the lack of a proper substrate, cover, flow, depth, pools, riffles, and the like, unrelated to water quality, prevent attainment of aquatic protection uses.

- Controls more stringent than those required by CWA sections 301(b) and 306 would result in substantial and widespread economic and social impact.

In addition to citing one or more of these factors to support removal of a use, states and authorized tribes use the same six factors to guide analysis and decision-making with respect to establishing an attainable use.

In all cases, states and authorized tribes must obtain scientifically sound data and information to make a proper assessment. It is also recommended that they conduct pollutant source surveys to define the specific dominant source of mercury in the waterbody. Sources may include point source loadings, air deposition, mining waste or runoff, legacy levels (e.g., mercury resulting from historical releases), and geologic "background levels." This is similar to source assessments under the TDML program. Existing documents provide guidance on obtaining data and conducting analyses for the other components of a UAA. These documents are at http://www.epa.gov/waterscience/standards/uaa/info.htm. The *Technical Support Manual: Waterbody Surveys and Assessments for Conducting Use Attainability Analyses* (USEPA 1983) covers the physical and chemical components of UAAs. Technical support for assessing economic and social impacts is offered through the *Interim Economic Guidance for Water Quality Standards Workbook* (USEPA 1995b).

EPA recognizes that there may be naturally occurring concentrations of methylmercury which may exceed the national recommended 304(a) criterion. However, EPA policy, whereby criterion may be set at ambient conditions if contaminant levels are due only to non-anthropogenic sources, applies only to aquatic life uses. The policy does not apply to human health uses. The policy states that for human health uses, where the natural background concentration is documented, this new information should result in, at a minimum, a re-evaluation of the human health use designation (USEPA 1997e).

4 Monitoring and Assessment

Water quality monitoring and assessment are essential elements in implementing the CWA at the local, state, and national levels. In implementing the water quality-based approach, the most obvious uses of monitoring information are in determining attainment of water quality standards and in developing TMDLs and permits. In the case of mercury, analyzing for mercury and methylmercury in water and fish is particularly important for states and tribes that choose to develop BAFs and methylmercury-to-mercury translators. This chapter provides guidance on analytical methods, field sampling, and assessment considerations for mercury. Additional information on developing site-specific BAFs and translators is provided in section 3.1.3 of this guidance.

4.1 What are the analytical methods for detecting and measuring mercury and methylmercury concentrations in fish and water?

Over the past two decades, EPA and other organizations have developed several analytical methods for determining mercury and methylmercury concentrations in fish and water. In 2001 EPA conducted a literature review to assess the availability of different analytical methods and to determine which of the analytical methods would be most useful for implementing the new methylmercury criterion. After the review, EPA concluded that nearly all current research on low-level concentrations of mercury and methylmercury is being performed using techniques that are based on procedures developed by Bloom and Crecelius (1983) and refined by Bloom and Fitzgerald (1988), Bloom (1989), Mason and Fitzgerald (1990), and Horvat et al. (1993).

To assist states and authorized tribes in selecting an analytical method to use, this chapter describes selected analytical methods available (sections 4.1.1 and 4.1.2), and identifies five specific methods that EPA recommends for use in implementing this guidance (section 4.1.3). In addition, appendix C of this document presents a list of available methods in more detail. Table C1 of the appendix summarizes 4 methods to analyze mercury and methylmercury in fish tissue, and table C2 summarizes 18 methods for the analysis of mercury and methylmercury in water and other nontissue matrices. Each table identifies the forms and species of mercury targeted by each method, estimated or known sensitivity, the techniques employed in the method, and any known studies or literature references that use the techniques employed in the method.

The CWA establishes an EPA approval process for certain methods used in the NPDES program and for section 401 certifications. As described in section 4.1.2 below, EPA has approved two of the above methods for analysis of mercury in water under 40 CFR part 136: method 1631, revision E and method 245.7. EPA's regulations generally require that these methods be used whenever such analyses are required for the NPDES program and for CWA section 401 certifications issued by states and authorized tribes (40 CFR 136.1). Sections 7.4 and 7.5.1.1 of this guidance provide additional information on appropriate analytical methods for measuring mercury in water for NPDES permitting purposes.

There are no regulatory requirements for the use of particular methods in setting water quality standards, evaluating the attainment of standards, or developing TMDLs,

although any methods used need to be scientifically defensible. Although this chapter provides recommendations for methods that can be used for these purposes, states and tribes are not precluded from using other methods, including those in appendix C.

4.1.1 Analytical Methods for Methylmercury

For measuring methylmercury in water, EPA method 1630 (USEPA 2001d), developed by EPA's Office of Water, reflects the techniques developed by Bloom and Crecelius (1983) and refined by Bloom and Fitzgerald (1988), Bloom (1989), Mason and Fitzgerald (1990), and Horvat (1993). This method has a quantitation level of 0.06 ng/L.

Draft modifications to method 1630, described in table C1 (see appendix C) and in Horvat et al. (1993), allow for measurement of methylmercury in fish tissue as low as 0.001 to 0.002 mg/kg, well below the water quality criterion for methylmercury in tissue (0.3 mg/kg). EPA recommends using these techniques when direct measurements of methylmercury in fish tissue are desired.

Three additional methods for measuring methylmercury in water are listed in table C2 (see appendix C). These methods are UW-Madison's standard operating procedure, or SOP (Hurley et al. 1996), used by the Great Lakes National Program Office for its Lake Michigan Mass Balance Study; USGS Wisconsin-Mercury Lab SOPs 004 (DeWild et al. 2002), used by USGS and EPA in the Aquatic Cycling of Mercury in the Everglades study; and a recently released USGS method (DeWild et al. 2002). All these procedures are based on the same techniques and have detection limits of 0.01 ng/L, 0.05 ng/L and 0.04 ng/L, respectively.

Because the four methods are nearly identical test procedures, they are expected to produce very similar results with sensitivity as low as 0.01 to 0.06 ng/L in water. These levels are well below the expected range of water column concentrations associated with the methylmercury fish tissue criterion.

4.1.2 Analytical Methods for Mercury

For measuring low level mercury in water, EPA method 1631, revision E (USEPA 2002c), developed by EPA's Office of Water, reflects the techniques developed by researchers mentioned previously. It has a quantitation level of 0.5 ng/L. EPA made this revision to clarify method requirements, increase method flexibility, and address frequently asked questions. The revision includes recommendations for using the clean techniques contained in EPA's *Method 1669: Sampling Ambient Water for Trace Metals at EPA Water Quality Criteria Levels* (USEPA 1996a). The benefits of using method 1631 are that it has been fully validated, numerous laboratories are routinely using the method, and it is sensitive enough to measure at the water concentrations expected to be associated with the criterion. This method was approved in 2002 under 40 CFR part 136 for NPDES permitting and other purposes under the CWA (67 FR 65876).

In addition, EPA method 245.7 (USEPA 2005e), which has a quantitation level of 5.0 ng/L, was approved under part 136 in 2007 (72 FR 11200). Developed by EPA's Office of Water, method 245.7 is similar to EPA method 1631E because both methods require use of a cold-vapor atomic fluorescence spectrometry (CVAFS) detector to measure low levels of mercury. Method 245.7 has been validated in two EPA

laboratories, one university laboratory, and an interlaboratory validation study. Results from these studies indicate that the method is capable of producing reliable measurements of mercury at some toxic criteria levels (40 CFR 136).

Appendix A to method 1631 (64 FR 10596) details the researcher's techniques for determining total and dissolved mercury in tissue, sludge, and sediments. The appendix was developed for processing fish tissue samples to be analyzed for mercury using the previously validated and approved method 1631 analytical procedures. The procedures are expected to be capable of measuring mercury in the range of 0.002 to 5.0 mg/kg.

EPA recognizes that some users might find Method 1631 (appendix A) costly or difficult to implement. Appendix C summarizes three other methods available for analyzing mercury in fish tissue that are less costly and less difficult to implement, but they have not undergone the same extensive interlaboratory validation studies as Method 1631 (appendix A). Two are listed in table C1 (Methods 245.6 and 7474). The third—Method 7473 for analyzing mercury in water, listed in table C2—has been adapted by some users for analyzing mercury in fish tissue; this approach has been used to measure mercury in fish tissue to support state fish consumption advisories.

Because researchers have found that nearly all mercury in fish tissue is in the form of methylmercury (USEPA 2000c), EPA also suggests that analysis of tissue for mercury, as a surrogate for methylmercury, might be a useful means for implementing the methylmercury criterion. If mercury concentrations in tissue exceed the criterion, further investigation of the methylmercury component might be desired.

4.1.3 Summary of Recommended Analytical Methods

In summary, on the basis of the available information, EPA believes that the most appropriate methods for measuring low levels of mercury concentrations in the water column are method 1631, revision E (mercury in water by CVAFS) and method 245.7 (mercury in water by CVAFS). Likewise, EPA believes that the most appropriate method for measuring methylmercury concentrations in the water column is method 1630 (methylmercury in water by CVAFS), and the most appropriate methods for measuring mercury concentrations in fish tissue are appendix A to method 1631 (mercury in tissue by CVAFS) and modifications to method 1630 for handling tissues. EPA recommends these procedures for the following reasons:

- EPA developed methods 1631 and 1630 to support implementation of water quality criteria for mercury and methylmercury, respectively. Both are already in the appropriate EPA format and include all standardized quality control elements needed to demonstrate that results are reliable enough to support CWA implementation.

- EPA developed method 245.7 specifically to address state needs for measuring mercury at ambient water quality criteria levels, when such measurements are necessary to protect designated uses. In addition, it has been validated in two EPA laboratories, one university laboratory, and an interlaboratory validation study.

- EPA developed appendix A to method 1631 to support its National Study of Chemical Residues in Lake Fish Tissue. Appendix A provides information on

preparing a fish tissue sample for analysis using method 1631. The method was validated by Brooks Rand (USEPA 1998b) and was used by Battelle Marine Sciences to analyze more than a thousand tissue samples collected during EPA's national study (USEPA 2000d). Successful use of these techniques also has been widely reported in the literature. This history, combined with the fact that appendix A supplements the already well-characterized and approved method 1631, makes this method a good candidate for use with the new fish tissue criterion.

- Method 1630 already has been used in several studies, including EPA's Cook Inlet Contaminant Study (USEPA 2001e) and the Savannah River TMDL study (USEPA 2001f). The techniques described in the method and in the recommended method modifications also have been successfully applied in numerous studies described in the published literature. Furthermore, the procedures in method 1630 are nearly identical to those given in the USGS method and in the University of Wisconsin SOP (Hurley et al., 1996), listed in table C2. The University of Wisconsin SOP was used in EPA's Lake Michigan Mass Balance Study (USEPA 2001g).

Table 4 summarizes the recommendations discussed above.

Table 4. Recommended analytical methods for detecting and measuring low levels of methylmercury and mercury in fish tissue and water

Recommended for analysis of:	**Methylmercury…** (see section 4.1.1)	**Mercury…** (see section 4.1.2)
...in fish tissue (for additional available methods, see appendix C, table C1)	Method 1630 with draft modifications for tissue	Method 1631, draft Appendix A
…in water (for additional available methods, see appendix C, table C2)	Method 1630	Method 1631, revision E* Method 245.7*

*Approved under 40 CFR part 136. See sections 7.4 and 7.5.1.1 for further information on appropriate methods for NPDES permitting purposes.

4.2 What is the recommended guidance on field sampling plans for collecting fish for determining attainment of the water quality standard?

EPA has published guidance providing information on sampling strategies for a fish contaminant monitoring program in volume 1, *Fish Sampling and Analysis*, of a document series, *Guidance for Assessing Chemical Contaminant Data for Use in Fish Advisories* (USEPA 2000c). This guidance provides scientifically sound recommendations for obtaining a representative sample for issuing fish consumption advisories, and can be applied for obtaining a representative sample for determining attainment. The guidance also includes recommendations for quality control and quality assurance considerations. In all cases, states and authorized tribes should develop data quality objectives for determining the type, quantity, and quality of data to be collected (USEPA 2000e).

4.2.1 What fish species should be monitored?

EPA's fish sampling guidance (USEPA 2000c) provides recommendations for selecting finfish and shellfish species for monitoring to assess human consumption concerns. According to the guidance, the most important criterion for selecting fish is that the species are commonly eaten in the study area and have commercial, recreational, or subsistence fishing value. States and tribes also should ensure that the species monitored reflect the fish species consumed by culturally and economically diverse communities. Fish creel data (from data gathered by surveying recreational fishers) from state fisheries departments are a justifiable basis for estimating types and amounts of fish consumed from a given waterbody. States and authorized tribes should ensure that the creel data are of sufficient quality and are representative of the local population of people that eat fish.

The fish sampling guidance also identifies recommended target species for inland fresh waters and for Great Lakes waters. Walleye and largemouth bass have been identified as freshwater fish that accumulate high levels of methylmercury. Reptiles, such as turtle species and alligators, are recommended as target species for mercury if they are part of the local diet. Larger reptiles can also bioaccumulate environmental contaminants in their tissues from exposure to contaminated sediments or consumption of contaminated prey.

The fish sampling guidance further recommends that the size range of the sampled target fish ideally should include the larger fish individuals harvested at each sampling site because larger (older) fish within a population are usually the most contaminated with methylmercury (Phillips 1980, Voiland et al. 1991). In addition, the methylmercury concentrations in migratory species are likely to reflect exposures both inside and outside the study area, and the state or authorized tribe should take this into account when determining whether to sample these species. For migratory species, EPA's fish sampling guidance recommends that neither spawning populations nor undersized juvenile stages be sampled in fish contaminant monitoring programs (USEPA 2000c). States and authorized tribes should consider the life history of migratory species and the consumption patterns of the local population when including migratory species in their fish sampling protocols. Sampling of target finfish species during their spawning period should be avoided because contaminant tissue concentrations might decrease at that time.

If states and authorized tribes do not have local information about the types of fish that people eat, the following two options provide an alternative for identifying which fish to sample:

- *Match assumed or known consumption pattern to sampled species.* If the state has some knowledge of the fish species consumed by the general population or by individuals in another target population, a monitoring sample could be composited to reflect this knowledge. For example, a state might decide that 75 percent of the fish consumed are trophic level 4 species, 20 percent are trophic level 3 species, and 5 percent are trophic level 2 species. A composite sample (see section 4.2.2) would reflect the determined trophic level breakout.

- *Use trophic level 4 fish only.* Predator species (e.g., trout, walleye, largemouth bass, and smallmouth bass) are good indicators for mercury and other persistent pollutants that are biomagnified through several trophic levels of the food web. Increasing mercury concentrations correlate with an increase in fish age, with some

variability, so that consumption of larger (older) individuals correlates with greater risks to human health. Increasing mercury concentrations also correlate with higher trophic levels, and thus consumption of higher-trophic-level species would provide greater risks to human health. Therefore, targeting trophic level 4 species should serve as a conservative approach (depending on the species most frequently consumed by recreational fishers) for addressing waterbodies with highly varying concentrations of methylmercury.

4.2.2 What sample types best represent exposure?

EPA recommends using composite samples of fish fillets from the types of fish that people in the local area eat because methylmercury is found primarily in fish muscle tissue (USEPA 2002c). Using skinless fillets is a more appropriate approach for addressing mercury exposures for members of the general population and most recreational fishers because fish consumers typically eat the fillets without skin. Because mercury is differentially concentrated in muscle tissue, leaving the skin on the fish fillet actually results in a lower mercury concentration per gram of skin-on fillet than per gram of skinless fillet (USEPA 2000c). Analysis of skinless fillets might also be more appropriate for some target species, such as catfish and other scaleless finfish species. Some fish consumers, however, do eat fish with the skin on. In areas where the local population eats fish with the skin or eats other parts of fish, the state or authorized tribe should consider including these parts of fish in the sample.

Composite samples are homogeneous mixtures of samples from two or more individual organisms of the same species collected at a site and analyzed as a single sample. Because the costs of performing individual chemical analyses are usually higher than the costs of sample collection and preparation, composite samples are most cost-effective for estimating average tissue concentrations in target species populations. In compositing samples, EPA recommends that composites be of the same species and of similar size so that the smallest individual in a composite is no less than 75 percent of the total length (size) of the largest individual (USEPA 2000c). Composite samples can also overcome the need to determine how nondetections will be factored into any arithmetical averaging because the composite represents a physical averaging of the samples. However, depending on the objectives of a study, compositing might be a disadvantage because individual concentration values for individual organisms are lost. *Guidance for Assessing Chemical Contaminant Data for Use in Fish Advisories,* volume 1, at sections 6.1.1.6 and 6.1.2.6, provides additional guidance for sampling recommendations.

4.2.3 What is the recommended study design for site selection?

Ideally, states and authorized tribes should collect samples over a geographic area that represents the average exposure to those who eat fish from the waterbody. However, if there are smaller areas where people are known to concentrate fishing, those areas should be used as the sampling area. Fish sampled in locations with mercury point sources should be included in the average concentration if fishing occurs in those areas but not included if the areas are not used for fishing.

Once the state or tribe identifies the geographic area, EPA recommends that they use a probabilistic sampling design to select individual sites or sampling locations. Use of a

probabilistic design can address the spatial variability of methylmercury levels in fish. This approach allows statistically valid inferences to be drawn about tissue levels in the area as a whole. EPA's *Guidance on Choosing a Sampling Design for Environmental Data Collection, for Use in Developing a Quality Assurance Project Plan* (USEPA 2002d) contains information about probabilistic site selection.

4.2.4 How often should fish samples be collected?

EPA's *Guidance for Assessing Chemical Contaminant Data for Use in Fish Advisories,* volume 1 (USEPA 2000c), at section 6.1.1.5, provides recommendations for how frequently to sample fish tissue. If program resources are sufficient, this guidance recommends biennial sampling of fish in waterbodies where recreational or subsistence harvesting is commonly practiced. If biennial screening is not possible, waterbodies should be screened at least once every five years. Also, the state or authorized tribe should sample during the period when the target species is most frequently harvested or caught.

In fresh waters, the guidance recommends that the most desirable sampling period is from late summer to early fall (August to October). Water levels are typically lower during that time, simplifying collection procedures. Also, the fish lipid content is generally higher, allowing the data to also provide information for other contaminant levels. The guidance does not recommend the late summer to early fall sampling period if it does not coincide with the legal harvest season of the target species or if the target species spawns during that period. In estuarine and coastal waters, the guidance recommends that the most appropriate sampling time is during the period when most fish are caught and consumed (usually summer for recreational and subsistence fishers).

EPA recommends that states and authorized tribes sample consistently in a season to eliminate seasonal variability as a confounding factor when analyzing fish monitoring data. Moreover, focused seasonality studies could be used both to assess the impact of seasonal variability on fish concentrations and to normalize concentrations to a standard season(s). Several studies have measured seasonality in the mercury concentrations in fish fillet muscle in estuaries and reservoirs (Kehrig et al. 1998; Park and Curtis 1997; Szefer et al. 2003). In these studies, concentrations were generally higher in cold seasons than in warm seasons by as much as two to three times. Slotten et al. (1995) showed that the uptake of methylmercury in zooplankton and fish increased dramatically during the fall mixing of Davis Creek Reservoir, a California reservoir contaminated by mercury mining activities.

No studies of seasonality of mercury concentrations in fish were found for rivers or natural lakes. On the basis of literature-reported fish mercury depuration rates, EPA does not expect seasonal fluctuations in fish mercury levels. Though reported mercury elimination half-lives cover a wide range of rates, from a few days to several years, the central tendency is 100–200 days (Burrows and Krenkel 1973; Giblin and Massaro 1973; Huckabee et al. 1979 [literature review]; McKim et al. 1976; Rodgers and Beamish 1982). Such slow depuration rates are expected to dampen strongly any fluctuations in methylmercury concentrations in fish. Instead, seasonal variations in fish tissue are likely linked to seasonal nutrition variability that affects fish body conditions but not mercury body burden.

4.2.5 How many samples should be collected?

EPA's *Guidance for Assessing Chemical Contaminant Data for Use in Fish Advisories, v*olume 1 (USEPA 2000c), at section 6.1.2.7.2, provides information to help determine the number of composite samples needed for comparing fish tissue information to a target value. The guidance does not recommend a single set of sample size requirements (e.g., number of replicate composite samples per site and number of individuals per composite sample) for all fish contaminant monitoring studies, but rather presents a more general approach that is both scientifically defensible and cost-effective. The guidance provides the means for determining an optimal sampling design that identifies the minimum number of composite samples and of individuals per composite necessary to detect a minimum difference between a target (in this case, the water quality criterion) and the mean concentration of composite samples at a site. Under optimal field and laboratory conditions, at least two composite samples are needed at each site to estimate the variance. To minimize the risk of a destroyed or contaminated composite sample's preventing the site-specific statistical analysis, at least three replicate composite samples should be collected at each site.

4.2.6 What form of mercury should be analyzed?

Because of the higher cost of methylmercury analysis (two to three times greater than that for mercury analysis), one approach for the states and authorized tribes could be to first measure mercury in fish tissue. States and tribes may find that more labs have the capability for mercury analysis and that the analysis time may be quicker.

When measuring only mercury, the state or authorized tribe might make the conservative assumption that all mercury in fish tissue is methylmercury. Appendix A summarizes eight studies of the relative proportion of the mercury concentration in North American freshwater fish that is in the form of methylmercury. In six of the eight studies, methylmercury, on average, accounted for more than 90 percent of the mercury concentration in fish tissue. In the remaining two studies, methylmercury, on average, accounted for 80 to 90 percent of the mercury concentration in trophic level 3 and 4 fish. If the measured mercury level exceeds the methylmercury criterion, states and tribes may wish to repeat the sampling (if sufficient tissue is not left) and analyze for methylmercury.

4.2.7 Other sampling considerations

EPA recommends that states and tribes routinely collect both weight and length data when assessing the potential influence of fish nutritional state on mercury concentration, and potentially for normalizing fish concentrations to a standard body condition. Greenfield et al. (2001), Cizdziel et al. (2002, 2003), and Hinners (2004) reported a negative correlation between fish body condition (a ratio of weight to cubed length) and fish tissue mercury concentration. Regardless of the exact mechanism, body condition offers a useful method to explain variability in fish mercury.

4.3 How should waterbody impairment be assessed for listing decisions?

Section 303(d)(1) of the CWA and EPA's implementing regulations require states and authorized tribes to identify and establish priority ranking for waters that do not, or are not expected to, achieve or maintain water quality standards. In accordance with this ranking, a TMDL for such waters must then be established. For purposes of determining impairment of a waterbody and whether to include it on section 303(d) lists, or in category 5 of the Integrated Report under sections 303(d) and 305(b)[15], states and authorized tribes must consider all existing and readily available data and information (see 40 CFR 130.7).

States and authorized tribes determine attainment of water quality standards by comparing ambient concentrations to the numeric and narrative AWQC (40 CFR 130.7 (b)(3)). Where a fish tissue criterion has been adopted, states and tribes should consider observed concentrations in fish tissue in comparison to the criterion. Where a water column translation of the fish tissue criterion has been developed and is adopted as part of the state's or tribe's water quality standards, states and tribes should consider ambient water concentrations in comparison to the translation.

For assessment of concentrations in fish tissue, resources may typically be unavailable to collect an adequate number of replicate composite samples to support rigorous statistical testing, especially where it is desirable to evaluate each individual target species separately. In these situations, states should make direct comparisons between composite sample concentrations and the criterion, as each composite effectively represents the average concentration observed in several fish.

Statistical tests for comparing the average concentration from multiple replicate composite samples to the criterion may be conducted where a sufficient number of replicates have been collected. EPA's *Guidance for Assessing Chemical Contaminant Data for Use in Fish Advisories*, volume 1 (USEPA 2000c), at section 6.1.2.7.2, recommends using the t-test to determine whether the mean concentration of mercury in composite fish tissue samples exceeds the screening value. This test involves a statistical comparison of the mean of all fish tissue data to the criterion. States and authorized tribes can evaluate whether the t-test statistic of the mean exceeds the water quality standards. This procedure could also be used to determine impairment, provided it is consistent with a state's water quality standards. States and authorized tribes might also want to consider the guidance in appendixes C and D of the *Consolidated Assessment and Listing Methodology*: *Toward a Compendium of Best Practices* (USEPA 2002e). Ultimately, the method that states and authorized tribes choose depends on how they express their water quality standards and apply their water quality assessment methodology.

4.3.1 How should nondetections be addressed?

When computing the mean of mercury in fish tissue, a state or authorized tribe might encounter a data set that includes analyzed values below the detection level. EPA does

[15] See EPA's guidance for Integrated Reports described at http://www.epa.gov/owow/tmdl/2006IRG/.

not expect this to occur frequently for two reasons. First, if the samples are physically composited (see section 4.2.2.), the composite itself provides the average, and there is no need to mathematically compute an average. Second, the newer analytical methods 1630 and 1631 can quantify mercury at 0.002 mg/kg, which should be lower than the observed mercury in most fish tissue samples being analyzed.

If, however, a state or authorized tribe is mathematically computing an average of a data set that includes several values below the detection level, the water quality standards and/or assessment methodology should discuss how it will evaluate these values. The convention recommended in EPA's *Guidance for Assessing Chemical Contaminant Data for Use in Fish Advisories*, volume 1, at section 9.1.2, is to use one-half of the method detection limit for nondetects in calculating mean values (USEPA 2000c). The guidance also recommends that measurements that fall between the method detection limit and the method quantitation limit be assigned a value of the detection limit plus one-half the difference between the detection limit and the quantitation limit. EPA notes, however, that these conventions provide a biased estimate of the average concentration (Gilbert 1987) and, where the computed average is close to the criterion, might suggest an impairment when one does not exist or, conversely, suggest no impairment when one does exist.

States or authorized tribes can calculate the average of a data set that includes values below the detection level using other statistical methods (e.g., sample median and trimmed means) (Gilbert 1987). EPA has published a review of several methods and analyzed the potential bias each can introduce into the calculation of the mean (USEPA 2001h).

One approach that a state or authorized tribe could take is to conduct a sensitivity analysis to ascertain the consequence of what value is used to quantify samples below the detection level. In a sensitivity analysis, the state or authorized tribe would compute the mean concentration by first using the value of the detection level to quantify samples below the detection level and then using a zero value for samples below the detection level. If both calculated means are above or below the criterion, it is clear that the choice of how to quantify samples below the detection level does not affect the decision. However, if one calculated mean is below the criterion and the other is above, it is clear that the choice of how to quantify samples below the detection level does affect the decision, and a more sophisticated approach such as the ones in *Robust Estimation of Mean and Variance Using Environmental Data Sets with Below Detection Limit Observations* (USEPA 2001h) should be used.

All methods have advantages and disadvantages. A state or authorized tribe should understand the consequences of which method it uses, especially if the choice makes a difference as to whether a waterbody is considered impaired or not. Furthermore, a state or authorized tribe should be clear about which approach it used. Again, the selected methodology must be consistent with the state's water quality standards and their published assessment method.

4.3.2 How should data be averaged across trophic levels?

If target populations consume fish from different trophic levels, the state or authorized tribe should consider factoring the consumption by trophic level when computing the average methylmercury concentration in fish tissue. To take this approach, the state or authorized tribe would need some knowledge of the fish species consumed by the general population so that the state or authorized tribe could perform the calculation using only data for fish species that people commonly eat. (For guidance on gathering this information, see section 3.2.1.2.) States and authorized tribes can choose to apportion all the fish consumption, either a value reflecting the local area or the 17.5 grams fish/day national value for freshwater and estuarine fish if a local value is not available, to the highest trophic level consumed for their population or modify it using local or regional consumption patterns. Fish creel data from state fisheries departments are one reasonable basis for estimating types and amounts of fish consumed from a given waterbody. The state or authorized tribe must decide which approach to use.

As an example of how to use consumption information to calculate a weighted average fish tissue concentration, see table 5 and equation 4.

Table 5. Example data for calculating a weighted average fish tissue value

Species	Trophic level	Number of samples	Geometric mean methylmercury concentration (mg/kg)
Cutthroat trout	3	30	0.07
Kokanee	3	30	0.12
Yellow perch	3	30	0.19
Smallmouth bass	4	95	0.45
Pumpkinseed	3	30	0.13
Brown bullhead	3	13	0.39
Signal crayfish	2	45	0.07

These concentrations are used to compute a weighted average of tissue methylmercury concentrations for comparison to the 0.3 mg/kg criterion. All fish measured are classified as trophic level 3 except signal crayfish, which are trophic level 2, and smallmouth bass, which are trophic level 4. The mean methylmercury concentration in trophic level 3 fish in this example is 0.15 mg/kg. This is calculated by weighting the geometric mean methylmercury concentration in each trophic level 3 species by the number of samples of each of the trophic level 3 species, and then averaging the weighted geometric means. Had the concentrations been averaged without weighting for the number of samples, the average concentration would have been 0.18 mg/kg and would have given more weight to the methylmercury concentrations in brown bullhead than to the concentrations in the other species. (Note that this averaging approach does not consider that the trophic level 3 fish in this sample are of different sizes, or that some fish might be consumed more or less frequently than is represented by the number of samples.) Equation 4 shows how the total (all trophic levels) weighted concentration is calculated using the 0.15 mg/kg value as representative of trophic level 3 fish and the default consumption for each trophic level:

$$C_{avg} = \frac{3.8 * C_2 + 8.0 * C_3 + 5.7 * C_4}{(3.8 + 8.0 + 5.7)} = 0.23 \text{ mg/kg} \qquad \text{(Equation 4)}$$

Where:

C_2 = average mercury concentration for trophic level 2
C_3 = average mercury concentration for trophic level 3
C_4 = average mercury concentration for trophic level 4

This calculation is based on apportioning the 17.5 grams/day national default consumption rate for freshwater and estuarine fish and shellfish by trophic level (5.7 grams/day of trophic level 4 fish, 8.0 grams/day of trophic level 3 fish, and 3.8 grams/day of trophic level 2 fish[16]). As noted throughout this document, however, the consumption pattern of the target population should be used if available.

If fish tissue concentration data from a trophic level are missing, one would drop the consumption factor for that trophic level from both the numerator and denominator. For example, if there were no tissue concentration data for trophic level 2 fish in the previous example, equation 5 shows the revised calculation:

$$C_{avg} = \frac{8.0 * C_3 + 5.7 * C_4}{(8.0 + 5.7)} = 0.27 \text{ mg/kg} \qquad \text{(Equation 5)}$$

This revised calculation preserves the relative contribution of each trophic level to consumption patterns. This approach (i.e., dropping a trophic level from Equation 4), however, should not be used if there are no fish tissue data for trophic level 4 fish. Since level 4 fish are the type of fish that people most often consume, dropping trophic level 4 from Equation 4 may result in underprotection if trophic level 4 fish are actually consumed at the site. Instead, the state or authorized tribe should collect information to determine the consumption rate for fish in trophic level 4. If the state or authorized tribe finds that no trophic level 4 fish are eaten, the state or tribe may drop trophic level 4 from Equation 4.

If the state or authorized tribe has developed a site-specific fish consumption rate for the criterion, the state or authorized tribe should incorporate this site-specific rate into equation 4. In this case, the state or authorized tribe would replace the values of 5.7 grams/day of trophic level 4 fish, 8.0 grams/day of trophic level 3 fish, and 3.8 grams/day of trophic level 2 fish with the values that the state or authorized tribe developed.

As an alternative approach, states or authorized tribes might wish to translate fish tissue sample data to a standard size, length, or species of fish that is more commonly consumed or is representative of the risk considerations of the state. Regression models

[16] The values for each trophic level are the same as those discussed in section 3.2.1.2; they can be found in *Methodology for Deriving Ambient Water Quality Criteria for the Protection of Human Health* (USEPA 2000b).

have been developed for this purpose (Rae 1997; Wente 2003). An inherent assumption is that concentrations will differ between samples of two different species/lengths/sample cuts in a fixed equilibrium distribution relationship among all fish. If this relationship is known and at least one tissue sample concentration is measured from a species/length/sample cut that is accurately described by this relationship, fish consumption risk analyses could be performed for any species/lengths/sample cuts described by the relationship at this site.

Such regression models may include independent variables that account for species, aquatic environment (e.g., lotic vs. lentic, or other waterbody characteristics), sample cut (e.g., whole fish, skin-on fillet, skinless fillet), specific characteristics (e.g., age and retention time) of reservoirs, temporal trends, and fish length. The response variable is fish mercury concentration, which is typically assumed to be lognormally distributed. In a graphic sense, the model shows the covariance of each combination of nominal scale variables (e.g., whole fish, lentic waterbody) with fish length, with the slope representing the concentration/length ratio. Regression slopes can vary from lake to lake, resulting in models that inappropriately retain some fish size covariation (Soneston 2003).

EPA used the USGS National Descriptive Model for Mercury in Fish Tissue in various analyses (USEPA 2005a). This model is a statistical model related to covariance, and it allows the prediction of methylmercury concentrations in different species, cuts, and lengths of fish for sampling events, even when those species, lengths, or cuts of fish were not sampled during those sampling events. The model can also prove useful to states and authorized tribes in averaging fish tissue across trophic levels.

4.3.3 How should older data be assessed?

For purposes of determining waterbody impairment and inclusion on section 303(d) lists or category 5 of the Integrated Report, states and authorized tribes must consider all existing and readily available water quality-related data and information (40 CFR 130.7). Ideally, a state or authorized tribe would have collected fish tissue information within the past five years, as recommended in section 4.2.4. Such recent information might not always be available, however, and the available data often includes mercury samples collected and analyzed several years in the past. When the state or authorized tribe evaluates this information, it should take into account the reliability of this information and its compliance with applicable data collection or quality assurance/quality control program requirements.

4.3.4 How should fish consumption advisories be used to determine impairment?

On October 24, 2000, EPA issued guidance on the use of fish advisories in CWA section 303(d) listing and 305(b) reporting decisions (USEPA 2000j). This guidance notes EPA's general interpretation that fish consumption advisories on the basis of waterbody-specific information can demonstrate impairment of CWA section 101(a) "fishable" uses. Although the CWA does not explicitly direct the use of fish consumption advisories to determine attainment of water quality standards, states and authorized tribes must consider all existing and readily available data and information to identify impaired waterbodies on their section 303(d) lists. For purposes of determining waterbody

impairment and inclusion on a section 303(d) list or in an Integrated Report, EPA considers a fish consumption advisory and the supporting data existing and readily available data and information.

When listing waters under CWA sections 303(d) or in the Integrated Reporting format on the basis of a fish advisory for a migratory fish species, the state or authorized tribe should include the waters the migratory fish are known to inhabit because those are the waters where the fish potentially would be exposed to mercury. In addition, a state or authorized tribe has the discretion to include any other water having a fish consumption advisory as impaired on its section 303(d) list if the state or authorized tribe believes inclusion is appropriate.

A state or authorized tribe should include on its section 303(d) list or in its Integrated Report, at a minimum, those waters for which waterbody-specific data that were the basis of a fish or shellfish consumption advisory demonstrate nonattainment of water quality standards. EPA believes that a fish or shellfish advisory demonstrates nonattainment when the advisory is based on tissue data, the data are from the specific waterbody in question, and the risk assessment parameters of the advisory or classification are cumulatively equal to or less protective than those in the water quality standards.[17]

For example, consider a state or authorized tribe that bases its water quality criterion on eating two fish meals a month. If the state or authorized tribe finds fish tissue information showing that the level of mercury is at a level where it decides to advise people not to eat more than one fish meal a month and all other risk assessment factors are the same, the advisory also may serve to demonstrate a water quality standard exceedance and that the waterbody should be placed on the 303(d) list or in the Integrated Report. In contrast, if this same state or authorized tribe finds the level of mercury in fish in another waterbody is at a level at which it would advise people to eat no more than three meals a month, and all other risk assessment factors are the same, the advisory is not necessarily the same as an impairment and the waterbody might not need to be listed.

[17] The October 2000 EPA guidance assumes that the fish tissue monitoring that supports the advisory is sufficiently robust to provide a representative sample of mercury in fish tissue. EPA's fish tissue guidance (USEPA 2000c) provides recommendations on how public health officials can collect sufficient information about contaminants in fish.

5 Other Water Quality Standards Issues

5.1 How does this criterion relate to the criteria published as part of the Great Lakes Initiative?

The 2001 recommended methylmercury fish tissue criterion and EPA's recommendations for its implementation do not supersede the requirements applicable to the Great Lakes at 40 CFR part 132. The Great Lakes regulatory requirements, known as the Great Lakes Initiative, or GLI, apply to all the streams, rivers, lakes and other bodies of water within the U.S. portion of the Great Lakes drainage basin. For those waters, a state or authorized tribe must adopt requirements (including water quality criteria) that are consistent with (as protective as) regulations EPA promulgated on March 23, 1995. See 60 FR 15366 and 40 CFR 132.1(b) and 132.4.

Under these regulations, if a state or authorized tribe adopts a fish tissue residue methylmercury criterion for the protection of human health, EPA, in its review of the new state or tribal criterion, must determine whether it is as protective as the mercury water column criterion for human health protection promulgated at 40 CFR 132.6, table 3, and whether all implementation procedures are as protective as the implementation procedure. See 40 CFR 132.5(g).

As described below, it is unlikely that adoption of EPA's 2001 recommended methylmercury fish tissue-based criterion of 0.3 mg/kg to protect human health would result in TMDLs or NPDES permit limits addressing mercury impairments in the Great Lakes basin less stringent than those that would be required under the existing GLI regulations. The reasons for this include the following:

- The GLI requires all states and authorized tribes to adopt the GLI wildlife water column criterion. The GLI wildlife criterion has a significantly more stringent methylmercury fish tissue basis than either the 2001 criterion or the GLI human health criteria and would therefore likely be the controlling basis for any TMDLs or NPDES permit limits addressing mercury pollution.

- Even if that were not the case, the 2001 criterion is more stringent than the methylmercury fish tissue basis for the GLI human health water column criteria for mercury.

Furthermore, using the 2001 fish tissue criterion would not necessarily result in lower transaction costs than the GLI. The GLI implementation procedures (e.g., the mixing zone prohibition, 40 CFR part 132, appendix F, procedure 3) require the use of water column criteria, so the 2001 methylmercury fish tissue criterion would need to be converted to a water column criterion following the GLI site-specific modification procedures before it could be approved by EPA and implemented using other GLI implementation procedures.

The human health criterion for mercury established by the GLI is 3.1 ng/L[18]. This water column criterion for mercury is equivalent to a methylmercury fish tissue residue value of 0.35 mg/kg using the Great Lakes-specific BAFs for mercury—27,900 L/kg for trophic level 3 and 140,000 L/kg for trophic level 4—as well as other Great Lakes-specific information (USEPA 1995c). Because EPA's 2001 methylmercury criterion (0.30 mg/kg) is more stringent than the GLI fish tissue residue value, the 2001 criterion would result in more stringent water column concentrations than the GLI human health criteria unless other, site-specific factors were significantly less stringent. This could occur, for example, if a state or authorized tribe applied the GLI site-specific modification procedures and found that the current, local BAF is significantly lower than the one used to develop the GLI criterion. In that case, the state or tribe could use the lower, local BAF and EPA's recommended fish tissue-based criterion to recalculate the water column criterion using the GLI site-specific modification procedures and submit it to EPA for review and approval. If the site-specific water column criterion was approved by EPA, the state or authorized tribe could use it and the GLI implementation procedures to develop TMDLs and NPDES permits.

Finally, as indicated above, if a state or authorized tribe were to adopt the 2001 human health criterion in the Great Lakes basin, this action most likely would not result in a change to TMDLs or NPDES permits. The GLI also includes a 1.3 ng/L criterion for the protection of wildlife, and in most instances, this more stringent criterion will drive the calculation of TMDLs or NPDES permit limits.

5.2 What is the applicable flow for a water column-based criterion?

If a state or authorized tribe adopts new or revised methylmercury criteria based on a water column value rather than a fish tissue value, it should consider the dilution flow specified in the state's or tribe's water quality standards when applying the new mercury criterion. Where a state's or authorized tribe's water quality standards do not specify the appropriate flow for use with the mercury criterion, EPA recommends using a harmonic mean flow. EPA used this flow for application of the human health criteria for mercury in the Great Lakes (40 CFR part 132). EPA also used this flow for application to the human health criteria in the National Toxics Rule (40 CFR 131.36) and the California Toxics Rule, or CTR (40 CFR 131.38). The Agency considers this flow to better reflect the exposure of fish to mercury. The technical means for calculating a harmonic mean is described in section 4.6.2.2.a of the *Technical Support Document for Water Quality-based Toxics Control* (USEPA 1991).

[18] EPA promulgated the GLI human health criteria of 1.8 ng/L in 40 CFR part 132, table 3, in March 1995, based on an RfD of 0.06 µg/kg/d. In May 1995 EPA revised the RfD to the current 0.1 µg/kg/d, which would result in GLI criteria of 3.1 ng/L. In October 1996 EPA issued guidance indicating that the 3.1 ng/L criteria were considered as protective as the promulgated 1.8 ng/L.

5.3 How are mixing zones used for mercury?

5.3.1 What is a mixing zone?

A mixing zone is the area beyond a point source outfall (e.g., a pipe) in which concentrations of a pollutant from a wastewater discharge mix with receiving waters. Under 40 CFR 131.13, states and authorized tribes may, at their discretion, include mixing zones in their water quality standards. Within a mixing zone, the water may be allowed to exceed the concentration-based water quality criterion for a given pollutant. The theory of allowing mixing zones is based on the belief that by mixing with the receiving waters within the zone, the concentration of the pollutant being discharged will become sufficiently diluted to meet applicable water quality criteria beyond the borders of that zone and fully protect the designated use of the waterbody as a whole. More information on mixing zones is available in the *Technical Support Document for Water Quality-based Toxics Control* (USEPA 1991) and the *Water Quality Standards Handbook* (USEPA 1994). States and authorized tribes often authorize mixing zone provisions and methodologies for calculating mixing zones for later application to NPDES point source discharge points.

5.3.2 How does a mixing zone apply for the fish tissue-based methylmercury criterion?

The question of mixing zones is not relevant when applying the fish tissue-based criterion, which refers to the level of mercury found in fish flesh. The criterion is fish tissue-based, not water column-based. The criterion reflects the exposure of the fish to mercury in the water column and food over the life of the fish, and thus it reflects an integration of the exposure over time and over spatially varying water column concentrations. The total load of mercury in the waterbody, taking into account the methylation rate and bioaccumulation of mercury in fish, affects the level of methylmercury in the fish tissue.

Some states and authorized tribes, however, might choose to adopt a water column criterion based on the fish tissue criterion and thus have a criterion for which a mixing zone might apply. In this situation, a state or authorized tribe should follow its existing procedures for determining appropriate mixing zones. EPA advises caution in the use of mixing zones for mercury. While fish tissue contamination tends to be a far field problem affecting entire waterbodies, rather than a narrow scale problem confined to mixing zones, EPA's guidance recommends restricting or eliminating mixing zones for bioaccumulative pollutants such as mercury so that they do not encroach on areas often used for fish harvesting (particularly for stationary species such as shellfish). Restriction or elimination might also be used to compensate for uncertainties regarding the ability of aquatic life or the aquatic system to tolerate excursions above the criteria, uncertainties inherent in estimating bioaccumulation, or uncertainties in the assimilative capacity of the waterbody. See the *Water Quality Standards Handbook*, section 5.1.3 (USEPA 1994).

5.3.3 Does the guidance for the fish tissue-based criterion change the Great Lakes Initiative approach to mixing zones for bioaccumulative pollutants?

To reduce the adverse effects from bioaccumulative chemicals of concern (BCCs) in the Great Lakes, on November 13, 2000, EPA promulgated an amendment to the Final Water Quality Guidance for the Great Lakes System (40 CFR part 132, appendix F, procedure 3). The regulation requires prohibition of mixing zones for bioaccumulative pollutants from existing discharges in the Great Lakes to the greatest extent technically and economically feasible. Specifically, existing discharges of BCCs are not eligible for a mixing zone after November 10, 2010 (although under certain circumstances mixing zones may be authorized). For new BCC discharges, the rule essentially prohibits mixing zones of bioaccumulatives immediately upon commencing discharge. This means that NPDES permit limitations for mercury discharged to the Great Lakes system must not exceed the water quality criterion. This also limits the flexibility that states and authorized tribes would otherwise have to adjust point source controls on the basis of nonpoint source contributions.

EPA reiterates that the new methylmercury criterion, and EPA's recommendations on its implementation, does not supersede the requirements applicable to the Great Lakes at 40 CFR part 132. The criteria for the Great Lakes are water column-based, and therefore they can be applied as an effluent requirement at the end of a pipe. EPA continues to view the prohibition of a mixing zone for mercury and other bioaccumulative pollutants for the Great Lakes as appropriately protective for water column-based water quality criteria applied to these waters.

If a state or authorized tribe adopts the new fish tissue-based criterion for a Great Lake or tributary to the Great Lake, the state or tribe would do this using the site-specific modification procedures of part 132 (see section 5.1 of this document). The state or tribe would have determined a site-specific BAF in this process and therefore would have the means for calculating a water column-based criterion. Under the part 132 regulations, EPA in its review of the new state or tribal implementation procedures would determine whether they are as protective as the Great Lakes procedures for human health protection (40 CFR 132.5(g)(3)). Specifically, EPA would determine whether the implementation procedures are as protective as applying the table 3 (in 40 CFR part 132) criterion for protection of human health without a mixing zone, consistent with the prohibition on mixing zones for BCCs (40 CFR 132, appendix F.3.c.). In addition, if the state's or tribe's implementation procedures involve converting the fish tissue-based criterion into an equivalent water column-based number, the mixing zone prohibition requirements of 40 CFR part 132 still apply.

5.4 How are fish consumption advisories and water quality standards harmonized?

5.4.1 What is the role of state and tribal Fish Advisory Programs?

States and authorized tribes have the primary responsibility of estimating the human health risks from the consumption of chemically contaminated, noncommercially caught finfish and shellfish (e.g., where water quality standards are not attained). They do this by

issuing consumption advisories for the general population, including recreational and subsistence fishers, and for sensitive subpopulations (such as pregnant women, nursing mothers and their infants, and children). These advisories are nonregulatory and inform the public that high concentrations of chemical contaminants, such as mercury, have been found in local fish. The advisories recommend either limiting or avoiding consumption of certain fish from specific waterbodies or, in some cases, from specific waterbody types (e.g., all lakes). In the case of mercury, many states and authorized tribes have calculated a consumption limit to determine the maximum number of fish meals per unit of time that the target population can safely eat from a defined area.

5.4.2 How are consumption limits for consumption advisories determined?

EPA has published guidance for states and authorized tribes to use in deriving their recommended fish consumption limits, titled *Guidance for Assessing Chemical Contaminant Data for Use in Fish Advisories*, volumes 1 and 2 (USEPA 2000c, 2000f). This guidance describes the two main equations necessary to derive meal consumption limits on the basis of the methylmercury RfD. Basically, the first equation is used to calculate the daily consumption limits of grams of edible fish (in g/day); a second equation is used to convert daily consumption limits to meal consumption limits over a specified period of time. Variables used to calculate the advisory consumption limits include fish meal size and frequency, consumer body weight, contaminant concentration in the fish tissue, the time-averaging period selected, and the reference dose for methylmercury health endpoints.

In the absence of site-specific fish consumption data, EPA recommends using a fish consumption rate of 17.5 grams/day of fish (uncooked) eaten from the local water as a screening level. This consumption rate equates to approximately two 8-ounce meals per month. Using this consumption rate, and assuming a 70-kg body weight (the same assumption used to derive the methylmercury criterion), the concentration of methylmercury in locally caught fish that would result in exposures that do not exceed the RfD (0.0001 mg/kg-day) is about 0.4 mg/kg and lower ([0.001 mg/kg-day x 70 kg bw]/0.0175 kg fish/day). This means that you can safely consume approximately two 8-ounce meals per month of locally-caught fish, where concentrations in such fish are 0.4 mg/kg or lower, and where there is no additional exposure (i.e., consumption of store bought or marine-caught fish).

Advisory limits can differ from one state or tribe to another. This inconsistency is due to a host of reasons, some of which speak to the flexibility states and authorized tribes have to use different assumptions (chemical concentrations, exposure scenarios and assumptions) to determine the necessity for issuing an advisory. The nonregulatory nature of fish advisories allows such agencies to choose the risk level deemed appropriate to more accurately reflect local fishing habits or to safely protect certain subpopulations (e.g., subsistence fishers).

5.4.3 How does the criterion differ from the advisory level?

Although EPA derived its recommended screening value for a fish advisory limit for mercury and human health methylmercury criterion from virtually identical

methodologies, it is important to clarify the distinctions between the two values. They are consistently derived, but because each value differs in purpose and scope, they diverge at the risk management level. Fish advisories are intended to inform the public about how much consumers should limit their intake of individual fish species from certain waterbodies. Alternatively, the Agency uses its methylmercury criterion, like other CWA section 304(a) criteria, as a basis for both nonregulatory and regulatory decisions. The criterion can serve as guidance to states and authorized tribes for use in establishing water quality standards, which, in turn, serve as a benchmark for attainment, compliance, and enforcement purposes.

The main risk management difference between EPA's recommended methylmercury water quality criterion and the fish advisory default screening value for mercury is that the criterion includes an RSC[19] and the screening value does not. In deriving the criterion, EPA assumed an RSC value of 2.7×10^{-5} mg/kg-day to account for exposure from marine fish and shellfish. The guidance for setting fish consumption limits also discusses using an RSC to account for exposures other than those from noncommercially caught fish, but the guidance may be applied without using an RSC. The RSC guidance in the 2000 Human Health Methodology (USEPA 2000b) provides more detail and specific quantitative procedures to account for other exposure pathways. EPA's advisory guidance recommends that states and authorized tribes consider using an RSC to account for exposure from other sources of pollutants (such as mercury) when deriving a fish consumption limit and setting a fish advisory for mercury.

5.4.4 What if there is a difference between assessing criterion attainment and issuance of a fish consumption advisory?

In many states and authorized tribes, numeric water quality criteria and fish and shellfish consumption limits differ because of inherent differences in the technical and risk assumptions used to develop them. As discussed in section 4.2, EPA considers a fish consumption advisory to demonstrate nonattainment of water quality standards when the advisory is based on tissue data, the data are from the specific waterbody in question, and the risk assessment parameters of the advisory or classification are cumulatively equal to or less protective than those in the water quality standards. Two situations in which the presence of an advisory might not imply an exceedance of the water quality standard (USEPA 2005f) are as follows:

- *Statewide or regional advisory.* States have issued statewide or regional warnings regarding fish tissue contaminated with mercury, on the basis of data from a subset of waterbodies, as a precautionary measure. In these cases, fish consumption advisories might not demonstrate that a CWA section 101(a) "fishable" use is not being attained in an individual waterbody and might not be appropriate for determining attainment based on exceedance of water quality criteria.

- *Local advisory.* States have issued local advisories using a higher fish consumption value than that which they use in establishing water quality criteria for protection of human health. Again, in this case the fish consumption advisories might not

[19] See discussion on the RSC in section 3.1.2.3 and 3.2.1.1.

demonstrate that a section 101(a) "fishable" use is not being attained in an individual waterbody and might not be as appropriate as comparison with water quality criteria as a basis for determining attainment.

For example, consider a state or authorized tribe that adopts EPA's methylmercury criterion of 0.3 mg/kg, which is based on eating approximately two 8-ounce fish meals a month. If the state or authorized tribe finds that a waterbody has fish with a mercury level of 0.2 mg/kg, this water would not be exceeding the water quality criterion. Yet, this mercury concentration is sufficient for the state or authorized tribe to issue a fish consumption advisory recommending that people eat no more than four 8-ounce meals a month. In this case, because the fish consumption advisory uses a higher fish consumption value than that used to develop the water quality criterion (and the fish tissue concentration does not exceed the criterion), consistent with EPA's 2000 guidance, the waterbody is not necessarily impaired (USEPA 2005f).

In the case where a local advisory is based on a higher fish consumption value which is considered representative of local consumption, the state or authorized tribe should consider whether it should adopt a site-specific criterion for the waterbody. A local advisory generally reflects actual contaminant monitoring data and may reflect local fish consumption patterns, and it might identify more representative fish species. The information gathered in developing the advisory might provide valid grounds for revising the level of a numeric water quality criterion to match that of the advisory.

5.4.5 Should existing advisories be revised to reflect the new criterion?

Although EPA's screening value for fish advisory studies and the recommended 304(a) criterion for mercury are based on similar methodologies and are intended to protect people who consume mercury-contaminated fish, they do not necessarily have to be the same value. As explained above, each limit is predicated on different risk-management decisions and thus incorporates different assumptions. However, recognizing that differences in consumption advisories and waterbody impairment for the methylmercury criterion can be confusing to the public, states may wish to consider explaining the differences in the information that these two types of listings provide. Likewise, there is merit in adopting a site-specific methylmercury criterion on the basis of a local fish advisory, if that advisory is supported by sufficient fish tissue and fish consumption data that are representative and of acceptable quality. Alternatively, states may wish to consider issuing a fish consumption advisory, where appropriate, if a waterbody is considered impaired based on the methylmercury 304(a) criterion and no such consumption warning exists.

5.4.6 What federal agencies issue advisories?

The Food and Drug Administration's (FDA's) mission is to protect the public health with respect to levels of chemical contaminants in all foods, including fish and shellfish, sold in interstate commerce. To address the levels of contamination in foods, FDA has developed both action levels and tolerances. An action level is an administrative guideline that defines the extent of contamination at which FDA may regard food as adulterated and represents the limit at or above which FDA may take legal action to

remove products from the marketplace. It is important to emphasize that FDA's jurisdiction in setting action levels is limited to contaminants in food shipped and marketed in interstate commerce; it does not include food that is caught locally by recreational or subsistence fishers. FDA also issues fish consumption advice on fish and shellfish sold in commerce in cases where contaminants have been detected at levels that may pose public health concerns for some consumers.

As described in section 5.4.2, EPA provides guidance to states, tribes, local governments and others on scientifically sound, cost-effective methods for developing and managing noncommercial fish consumption advisories on local waters. See EPA's *Guidance for Assessing Chemical Contaminant Data for Use in Fish Advisories* (USEPA 2000c, 2000f). In addition, EPA has issued advice under CWA section 104(b)(6) to supplement state and/or tribal advice on local waters.

In March 2004, EPA and FDA issued a joint national fish advisory about mercury in fish and shellfish. The purpose of the advisory is to inform women who may become pregnant, pregnant women, nursing mothers, and parents of young children how to get the positive health benefits from eating fish and be confident that they have reduced their exposure to the harmful effects of mercury. The 2004 advisory lists fish sold in interstate commerce that are known to be high in mercury as well as fish that that are low in mercury to help consumers choose the most appropriate fish. The advisory also contains recommendations about eating fish harvested from local waters where no advice has been provided by state or tribal authorities. Information regarding the national advisory is at http://www.epa.gov/waterscience/fish/.

5.4.7 How is the criterion related to FDA action levels?

The current FDA action level for mercury in fish is 1 mg/kg. Generally, an action level is different from a fish advisory limit—and even more different from a CWA section 304(a) criterion. FDA action levels are intended for members of the general population who consume fish and shellfish typically purchased in supermarkets or fish markets that sell products harvested from a wide geographic area. The underlying assumptions used in the FDA methodology were never intended, as local fish advisories are, to be protective of recreational, tribal, ethnic, and subsistence fishers who typically consume fish and shellfish from the same local waterbodies repeatedly over many years. EPA and FDA have agreed that the use of FDA action levels for the purposes of making local advisory determinations is inappropriate. Furthermore, it is EPA's belief that FDA action levels and tolerances should not be used as a basis for establishing a state's or tribe's methylmercury criterion.

5.5 What public participation is recommended for implementing the methylmercury criterion?

By applicable regulations, water quality standards, TMDL, and NPDES permit decisions require public notice and the opportunity for the public to comment on tentative decisions. Some public interest groups might have an interest in decisions related to mercury, especially in areas where local citizens rely heavily on locally caught fish as a food source. EPA recommends that organizations with an interest in environmental justice issues be included in the public notice.

6 TMDLs

6.1 What is a TMDL?

CWA section 303(d)(1) and EPA's implementing regulations require states and authorized tribes to identify and establish priority rankings for waters that do not, or are not expected to, achieve or maintain water quality standards with existing or anticipated required controls. This list is known as the state's or tribe's list of "impaired" waterbodies or 303(d) list. States and authorized tribes then must establish TMDLs for the impaired waterbodies.

A TMDL is a calculation of the maximum amount of a pollutant that a waterbody can receive and still meet water quality standards. A TMDL also allocates the pollutant loads among the contributing sources, both point and nonpoint. The TMDL calculation must include a margin of safety to take into account any uncertainty in the TMDL calculation and must account for seasonal variation in water quality. The current statutory and regulatory framework governing TMDLs includes CWA section 303(d) and the TMDL regulations published in 1985 at 40 CFR 130.2 and 130.7 and amended in 1992 (see 50 FR 1774 (Jan. 11, 1985); 57 FR 33040 (July 24, 1992)).

As of the 2008 303(d) listing cycle, 43 states and Puerto Rico reported at least one waterbody as impaired due to mercury, and more than 8,800 specific waterbodies were listed as impaired due to mercury, either solely or in combination with other pollutants. As mentioned previously in section 2.4, with the implementation of the new methylmercury fish tissue criterion, monitoring of previously unmonitored waterbodies, and use of more sensitive analytical methods, EPA expects that the number of waterbodies listed as impaired due to mercury might increase.

6.2 How have states and tribes approached mercury TMDLs?

Developing TMDLs for waters impaired by mercury raises a number of technical and policy issues. For example, air deposition is the predominant source of mercury to many waterbodies, especially in the eastern United States. The mercury deposited from air comes from local, regional, and international sources, and identifying how each of these sources contributes to the mercury load in the waterbody is challenging. In other waterbodies, significant loadings might come from other sources, such as past metal-mining activity or geologic sources. Frequently, states and authorized tribes do not have the authority to address all the sources that contribute mercury to their waterbodies and rely on efforts conducted under a variety of programs, such as regulations under the CAA, pollution prevention programs, and international efforts to reduce releases and emissions from mercury sources. States and EPA have found that, in many cases, it is important to coordinate closely with programs other than those under the CWA to address these mercury sources.

Given these challenges, EPA is working with states, tribes, and stakeholders to determine how best to use TMDLs and the 303(d) listing process to provide a basis for reducing mercury releases to water, including consideration of air deposition, to meet applicable

water quality standards and CWA goals. In areas where large numbers of waterbodies are impaired due to mercury derived from air deposition, some states have begun to explore ways to address mercury impairments efficiently, such as through development of TMDLs on various geographic scales. As of April 2010, mercury TMDLs have been approved for more than 6,700 waterbodies, including a "statewide" mercury TMDL in Minnesota and a multi-state mercury TMDL for the Northeast states (see below).

On March 8, 2007, EPA issued a memorandum describing a voluntary approach for listing waters impaired by atmospheric mercury under CWA section 303(d) and managing the development of mercury TMDLs. (USEPA 2007) (http://www.epa.gov/owow/tmdl/mercury5m/Mercury5m.pdf). EPA recommends this approach for states that have in place a comprehensive statewide mercury reduction program with elements recommended by EPA. These states may separate their waters impaired by mercury predominantly from atmospheric sources in a subcategory of their impaired waters list ("5m") and defer the development of TMDLs for those waters. A state using the 5m subcategory may continue to defer the development of mercury TMDLs where the state demonstrates continuing progress in reducing in-state mercury sources. Recommended elements of a mercury reduction program include identification of air and multimedia sources within a state and programs to address those sources; mercury reduction goals and target dates; multimedia monitoring; public reporting on the state's mercury reduction efforts; and multistate coordination. The 5m subcategory is intended to recognize states with comprehensive mercury programs and to allow states to focus on early implementation actions.

Because the 5m subcategory is focused primarily on waterbodies impaired by mercury from air deposition, EPA recommends that the 5m subcategory include waters where the proportion of mercury from air deposition is high compared to other mercury sources. In the 5m memorandum, EPA recommends that states describe how such waterbodies were identified. Such information will help determine whether the 5m approach is appropriate. EPA also believes that, as the relative contribution to a waterbody from sources other than air deposition increases, such as water point sources, it may be more appropriate to use the TMDL process to characterize and address those sources sooner, rather than deferring TMDL development. As stated in the 5m memorandum, states have the option to continue developing mercury TMDLs sooner, whether or not they place waterbodies in subcategory 5m.

On September 29, 2008, EPA issued a document titled *Elements of Mercury TMDLs Where Mercury Loadings Are Predominantly from Air Deposition*, to assist states, EPA regional staff, and other stakeholders in identifying approaches for the development of mercury TMDLs (USEPA 2008a). Compiled in a checklist format, approaches described in the document are drawn largely from approaches and best practices used in approved mercury TMDLs. The checklist summarizes considerations in addressing the required and recommended TMDL elements described in the *Guidelines for Reviewing TMDLs under Existing Regulations Issued in 1992* (USEPA 2002f) when developing mercury TMDLs on geographic scales ranging from waterbody-specific to multi-state.

While the checklist is based on existing guidance for reviewing TMDLs, this guidance document supplements the checklist by providing additional information and case studies on approaches that have been used in approved mercury TMDLs to date, and examples of

technical tools available to assist in mercury TMDL development. Technical tools available to assist in the development of mercury TMDLs include screening-level analyses of mercury loadings and sources using the Mercury Maps tool and more complex water and air models. Many of these tools are discussed in the sections below.

EPA recommends that states continue to develop TMDLs for mercury-impaired waters where appropriate, taking into account the considerations and approaches described in this guidance. States may also consider using the 5m subcategory for waters impaired by mercury predominantly from air deposition if the state has a comprehensive mercury reduction program as described in the 5m memorandum.

6.2.1 What geographic scales have been used for mercury TMDLs?

Many mercury TMDLs approved to date were developed on a waterbody-specific basis. They include some of the first approved mercury TMDLs, such as those developed for waterbodies in middle and south Georgia. Other examples include TMDLs developed for waterbodies in Louisiana, such as the Ouachita River, the Narraguinnup and McPhee reservoirs in Colorado, and Pena Blanca and Arivaca lakes in Arizona. Various aspects of these TMDLs are described further in appendix D.

In areas of the country where many waterbodies are listed as impaired due to mercury primarily from atmospheric sources, some states have begun to explore the development of mercury TMDLs on a watershed scale or on the basis of a large geographic area, such as a state or region. One example of a regional or grouped approach is the mercury TMDL for the Coastal Bays and Gulf Waters of Louisiana, approved in June 2005. The TMDL covers six segments of coastal Louisiana. Because of the large geographic extent of mercury in the coastal waters and the similar extent of mercury contributions from air deposition, the TMDL was developed on a watershed basis rather than waterbody by waterbody. The TMDL used air deposition modeling results from the Regional Modeling System for Aerosols and Deposition (REMSAD) to estimate wet and dry deposition of mercury for the six segments. The air deposition modeling results, in turn, were used to model runoff or nonpoint source mercury loadings. As described in the following section, mercury loadings can include direct deposition to waterbodies and deposition to the watershed that is subsequently transported to the waterbody via runoff and erosion. Additional information on this TMDL can be found on EPA's TMDL webpage at http://iaspub.epa.gov/tmdl/waters_list.tmdl_report?p_tmdl_id=11642.

A "statewide" mercury TMDL developed by Minnesota was approved by EPA on March 27, 2007. The TMDL report covers 998 mercury impairments and is the first approved mercury TMDL covering such a large number of waterbodies and large geographic area. (Note: Although called statewide, the TMDL does not cover all mercury-impaired waterbodies in the state.) Minnesota used a statewide approach because the predominant mercury source in those waterbodies—air deposition—is relatively uniform across the state. The final TMDL report includes two TMDLs—one for the northeast region of the state and the other for the southwest region of the state. Waterbodies were grouped into the two regions on the basis of differences in fish tissue concentrations, with higher fish mercury concentrations in the northeast region compared to the southwest region. The difference in mercury concentrations is thought to be due to the effect of land use and other factors on the methylation of mercury. For example, the

northeast region is dominated by wetlands, where mercury tends to be methylated more readily; the southwest is dominated by cultivated lands. A summary of the Minnesota mercury TMDL approach is provided in appendix D, and the allocation approach is described further below. The final TMDL and EPA decision document are at http://www.pca.state.mn.us/water/tmdl/tmdl-ercuryplan.html#approval.

On December 20, 2007, EPA approved the Northeast Regional Mercury TMDL covering waterbodies in Connecticut, Maine, Massachusetts, New Hampshire, New York, Rhode Island and Vermont. In using a regional approach, the TMDL document provides aggregate wasteload allocations and load allocations for the region. The regional approach was based on an analysis of data showing similar levels of mercury in fish throughout waterbodies in the region, and the states' finding that air deposition is the predominant mercury source. The TMDL document focuses on waters impaired by mercury primarily from atmospheric sources; it excludes coastal and marine waters and a few areas of high localized deposition and high fish mercury levels. The number of individual waterbodies covered by the regional TMDL document amounts to over 5,300 (the specific number of waterbodies covered by the TMDL document vary from state to state and are cited in EPA's approval documents). The TMDL target is EPA's recommended fish tissue criterion of 0.3 ppm methylmercury for each of the states except for Connecticut and Maine, where the targets are 0.1 ppm and 0.2 ppm, respectively. The TMDL allocates approximately 2.0 percent of the loading capacity to point sources and 98 percent to nonpoint sources (predominantly atmospheric deposition). The TMDL assumes that most of the reductions would need to come from atmospheric sources. The Northeast Regional Mercury TMDL are at http://www.epa.gov/region1/eco/tmdl/assets/pdfs/ne/Northeast-Regional-Mercury-TMDL.pdf, and the EPA approval documents for each of the states are at http://www.epa.gov/region1/eco/tmdl/approved.html.

6.2.2 What are the considerations in developing mercury TMDLs?

A TMDL must identify the applicable water quality standards for each listed segment and identify the loading capacity of a water (40 CFR 130.2). In addition, a TMDL must allocate the pollutant loads among the sources, both point and nonpoint (40 CFR 130.2(i)). EPA guidance further notes that a TMDL should identify the pollutant sources, both point and nonpoint, including the location of the sources and quantity of the loading. Where feasible, states are encouraged to consider waterbodies affecting disadvantaged communities and tribal issuses in setting priorities for TMDL development. Some of the considerations in developing a mercury TMDL and approaches used in approved mercury TMDLs are described in more detail in the text below.

6.2.2.1 What are potential mercury sources to waterbodies?

An important step in TMDL development is an evaluation of the loadings from various sources. The potential sources of mercury to waterbodies include the following: (1) direct discharges of mercury from water point sources, including industrial dischargers and wastewater treatment plants; (2) atmospheric deposition, including direct deposition to the waterbody surface and deposition to the watershed, which subsequently is transported to the waterbody via runoff and erosion, including via stormwater; (3) runoff, ground water flow, acid mine drainage, and erosion from mining sites or mining wastes, and

other waste disposal sites such as landfills and land application units; (4) sediments, which might have mercury contamination or hot spots resulting from past discharges; and (5) "naturally occurring" mercury in soils and geologic materials. Sediments containing mercury from past discharges might continue to contribute mercury to the overlying waterbody. Further discussion of each of these types of sources follows.

Point sources. Point source discharges of mercury include POTWs, electric utilities, and other industrial facilities. Sources of data on point source discharges of mercury include the Permit Compliance System, as well as a study of domestic mercury sources by the Association of Metropolitan Sewerage Agencies (AMSA 2000), now called the National Association of Clean Water Agencies (NACWA). Without accurate discharge data, a sample of a representative portion of dischargers has been used in mercury TMDLs to estimate the mercury discharges from point sources. In addition, some point source dischargers, such as chlor-alkali plants and POTWs, might have permits requiring monitoring for mercury, although most dischargers, especially smaller dischargers, are not likely to have such monitoring requirements. NPDES-permitted stormwater sources might also include mercury discharges, which in turn might include mercury originating from atmospheric deposition.

Atmospheric deposition. Deposition of mercury from the air can be a significant source of mercury in many waterbodies. Some waterbodies have been identified as receiving as much as 99 percent of their total loading from atmospheric deposition, either directly or indirectly via runoff and erosion. (See Ochlockonee, Georgia, TMDL in appendix D.) The mercury in atmospheric deposition originates from anthropogenic sources, including U.S. and international sources, as well as natural sources. Examples of specific anthropogenic sources that emit mercury to the air include medical and municipal waste incinerators, electric utilities, chlor-alkali plants, and active metals mining, among others.

Mercury is emitted to the air in several chemical forms or species. Common measurements of mercury in air differentiate between reactive gaseous mercury (RGM), elemental mercury (Hg^0), and particulate mercury (Hg_p). Some chemical forms of mercury emissions to air deposit relatively close to their sources, while others are transported over longer distances and even globally. The mix of chemical forms or species emitted from a given source determines what fraction of the mercury from that source is depositing locally and what proportion is transported over longer distances, making the task of identifying sources of deposition to a waterbody challenging. At any given location, the mercury deposited from air can originate from several sources. Figure 3 depicts the current understanding of deposition from U.S. and international sources. It shows that in many parts of the United States, the source of deposited mercury is not a U.S. source.

Of the approved mercury TMDLs involving atmospheric loadings, most have characterized the contributions from air deposition in terms of total or aggregate loadings. Atmospheric mercury loadings include both direct deposition to the waterbody surface and indirect deposition to the watershed. Indirect deposition is that which is deposited to the watershed and then transported to the waterbody via runoff and erosion. Atmospheric mercury loadings include both wet and dry deposition of mercury.

It is important to use the most current information about deposition because U.S. mercury emissions into the air have decreased over time. Older data on deposition might not reflect current deposition conditions. For example, figure 4 depicts a summary of U.S. mercury air emissions between 1990 and 2005 and shows a 58 percent overall decrease.

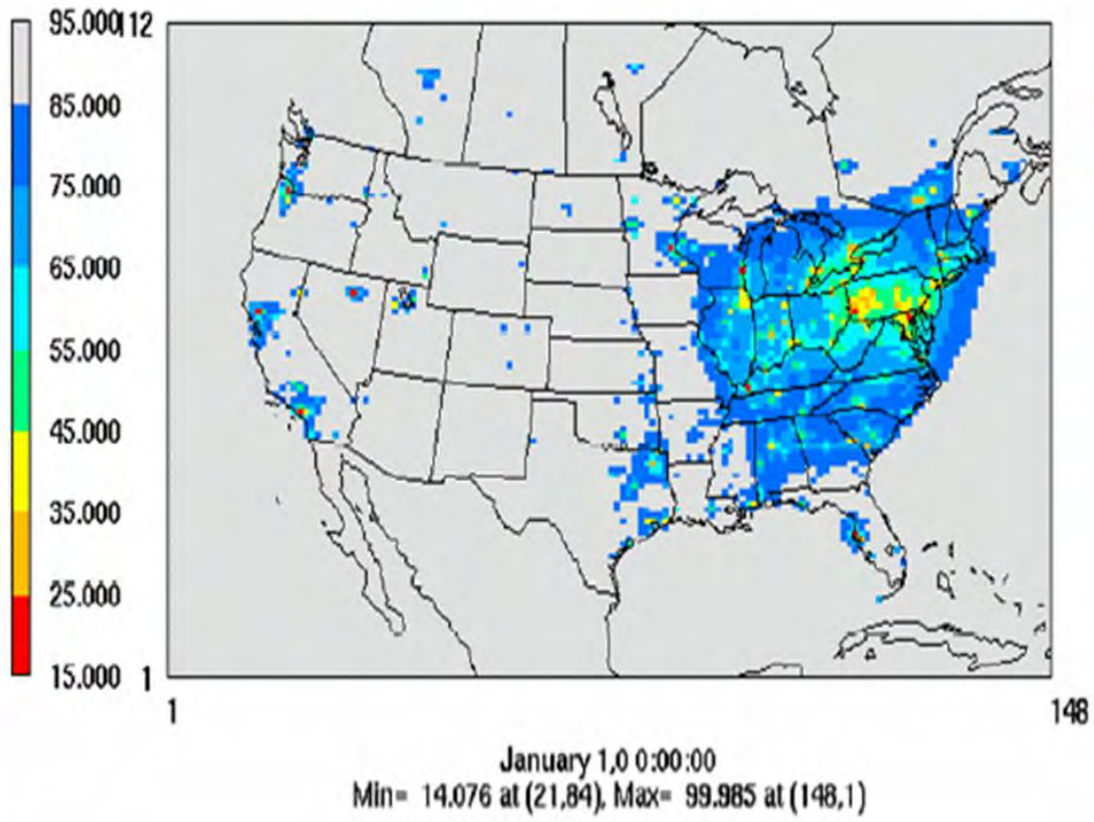
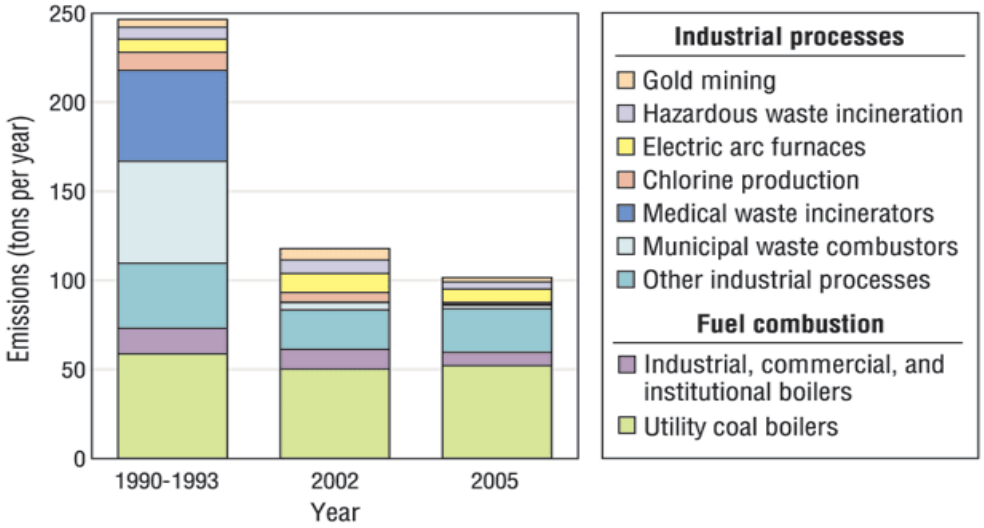


Figure 3. Percentage of total mercury deposition attributable to global sources (USEPA 2005a).

Exhibit 2-39. Mercury emissions in the U.S. by source category, 1990-1993, 2002, and 2005[a,b]



[a]1990-1993 is considered the baseline period for mercury emissions. The baseline period spans multiple years due to the availability of emissions data for various source categories. The data presented for the baseline period are annual emissions (tons per year) and are therefore comparable to the 2002 and 2005 data.

[b]Mercury emissions from mobile sources are not depicted because they have been estimated only for inventory years 2002 (0.8 tons) and 2005 (1.1 tons), not for the baseline period.

Data source: *U.S. EPA, 2009*

Figure 4. Trends in mercury air emissions between 1990 and 2005 (USEPA 2008b).

Additional decreases in mercury air emissions may have occurred since 2005 as the result of EPA's regulatory efforts under the CAA. At the same time, however, global emissions might have increased.

The 2005 National Emissions Inventory (NEI) is EPA's latest comprehensive national emission inventory. It contains emission measurements and estimates for 7 criteria pollutants and 188 hazardous air pollutants (HAPs). The NEI contains emissions for all major contributors to air pollution, including point sources (large industrial sources such as electric utilities and petroleum refineries), mobile sources (both onroad sources such as cars and trucks and nonroad engines such as those in construction equipment and agricultural equipment), and nonpoint sources (small stationary sources such as residential fuel use and various types of fires). The NEI includes emission estimates for the entire United States. For point sources, the NEI inventories emissions for each individual process at an industrial facility. For mobile and nonpoint sources, the NEI contains county-level emission estimates. The NEI is developed using the latest data and best estimation methods, including data from Continuous Emissions Monitors; data collected from all 50 states, as well as many local and tribal air agencies; and data generated using EPA's latest models such as the MOBILE and NONROAD models. More information on the 2005 NEI is at http://www.epa.gov/ttn/chief/net/2005inventory.html.

Some approved mercury TMDLs have identified the types or categories of sources likely to contribute to mercury deposition in a waterbody. An example of this type of source analysis is included in the Savannah River mercury TMDLs issued February 28, 2001, and a series of mercury TMDLs issued February 28, 2002, for a number of watersheds in middle and south Georgia (see http://gaepd.org/Documents/TMDL_page.html). These TMDLs included an analysis of the categories of air sources contributing deposition to the waterbodies and the reductions in loadings expected from controls in place when the TMDL was approved. To estimate the total contributions from air deposition, data from the Mercury Deposition Network (MDN) were used. Modelers also used the existing Regional Langrangian Model of Air Pollution (RELMAP) deposition results developed for the 1997 Mercury Report to Congress to estimate the relative contributions from local sources within a 100-kilometer airshed.

EPA has evaluated water and air deposition modeling tools as part of two mercury TMDL pilot projects in Wisconsin and Florida. In particular, the pilots examined approaches for combining the results of air deposition and water quality modeling, which in turn might be used in a TMDL context. In the Florida pilot, air modelers used a combination of modeling tools to predict the amount of mercury deposition to the study area from local sources in southern Florida. Using the Mercury Cycling Model, aquatic modelers then used results from the atmospheric modeling and other data to examine how mercury levels in fish might respond to reductions in deposition. The Florida pilot report is complete (see ftp://ftp.dep.state.fl.us/pub/labs/assessment/mercury/tmdlreport03.pdf) (Atkeson et al. 2002).

In the Wisconsin pilot project, EPA evaluated modeling tools such as the Regional Modeling System for Aerosols and Deposition (REMSAD) for identifying the sources or categories of sources contributing mercury deposition to a waterbody, as well as how to use the deposition results as input to aquatic models, similar to the approach used in the Florida pilot. REMSAD is a three-dimensional grid model designed to calculate the concentrations of both inert and chemically reactive pollutants by simulating the physical and chemical processes in the atmosphere that affect pollutant concentrations (ICF International 2006). REMSAD simulates both wet and dry deposition of mercury. (See appendix E for further information on REMSAD.) In the Wisconsin pilot, the results of the air deposition modeling were used as input to the Mercury Cycling Model to examine how mercury levels in fish might respond to potential changes in deposition.

Other TMDLs in which the results of REMSAD modeling were used include the mercury TMDL for the Coastal Bays and Gulf Waters of Louisiana approved in 2005. The results of earlier air modeling for the *Mercury Study Report to Congress* were used in the mercury TMDLs for middle and south Georgia approved in 2002 (see Ochlockonee TMDL in appendix D). EPA plans to provide each state or authorized tribe with modeled estimates of mercury deposition from sources within the state or on the tribal land and contributions from sources outside the state or tribe. The modeling results will help EPA and the states and authorized tribes develop TMDLs and determine the appropriate strategies for addressing mercury deposition from sources within their jurisdictions.

Additional tools available for determining mercury deposition loadings include the Community Multi-Scale Air Quality (CMAQ) model. The CMAQ modeling system is a comprehensive, three-dimensional, grid-based Eulerian air quality model designed to

estimate pollutant concentrations and depositions over large spatial scales (Dennis et al. 1996; Byun and Ching 1999; Byun and Schere 2006). The CMAQ model is a publicly available, peer-reviewed, state-of-the-science model with a number of science attributes that are critical for simulating the oxidant precursors and nonlinear chemical relationships associated with mercury formation. Version 4.3 of CMAQ (Bullock and Brehme 2002; Byun and Schere 2006) reflects updates to earlier versions in a number of areas to improve the underlying science and address comments from peer review. Further information on the CMAQ model is provided in appendix E.

As with any analysis based on limited data, uncertainty is inherent in the estimates of all analytical outputs of modeling. Model uncertainty results from the fact that models and their mathematical expressions are simplifications of reality used to approximate real-world conditions, processes, and their relationships. Models do not include all parameters or equations necessary to express real-world conditions because of the inherent complexity of the natural environment and the lack of sufficient data to describe the natural environment. Consequently, models are based on numerous assumptions and simplifications and reflect an incomplete understanding of natural processes. As a result, there will be some uncertainty when using models to quantify the sources of air-deposited mercury.

Other tools available to help states characterize mercury deposition include existing national monitoring networks and modeling tools, such as the MDN. Examples of these tools are provided in appendix F. Published results of national modeling studies could also be available to help estimate atmospheric deposition loadings. Further information on tools and approaches for characterizing atmospheric deposition to waterbodies can be found in the Frequently Asked Questions about Atmospheric Deposition section of EPA's Web site at http://www.epa.gov/oar/oaqps/gr8water/handbook/.

An analysis of deposition should take into account both direct deposition to the waterbody, as well as mercury deposited within the watershed (indirect deposition). In addition, fires, flooding, and other landscape disturbances could re-mobilize mercury previously deposited within the watershed and cause an increase in mercury transported to the waterbody. Studies are underway to examine the extent to which mercury deposited to a watershed is transported to a waterbody. For example, the Mercury Experiment to Assess Atmospheric Loading in Canada and the United States (METAALICUS) project is a mercury loading experiment to examine the timing and magnitude of the relationship between mercury loading to ecosystems and mercury concentrations in fish (Harris et al. 2006). Using stable mercury isotopes, researchers are examining the fate of mercury deposited to uplands, wetlands, and directly to lakes. It is being carried out at the Experimental Lakes Area (ELA) in northwestern Ontario by U.S. and Canadian researchers. A discussion of factors affecting mercury transport and bioavailability is included in chapter 2 of this guidance.

As part of a source evaluation, EPA encourages states to conduct a careful analysis to verify and quantify the contributions of air deposition as compared to other sources. Such information is important for determining the appropriate management approaches. For example, an analysis of the contribution from air sources is the basis for determining whether it may be appropriate to defer TMDLs under the 5m approach, or whether it is more appropriate to develop TMDLs to address significant local sources.

Although not required for a TMDL, states may wish to examine the contributions to the watershed from local air sources within the state as compared to out-of-state sources. Such information provides a basis for determining the appropriate allocations. In turn, such source information can help to develop a meaningful TMDL implementation plan and identify the extent to which state and local programs may be appropriate for addressing the mercury sources.

Metals mining activity. Loadings from metals mining activities might reflect both historical and recent mining activity within the watershed. Mining areas of interest are those involving "placer" deposits, in which mercury itself is present in the ore, or those deposits for which mercury is used to extract other metals such as gold. For example, sulfide replacement deposits are often associated with mercury. Locations at mining sites that might serve as sources of mercury include direct seeps, as well as leachate from tailings or spoil piles. In the Clear Lake TMDL (see appendix E), ground water from an abandoned mining site was reported to contain mercury that is readily methylated. In Clear Lake, acid mine drainage was found to contain high sulfate concentrations, which might enhance methylation by sulfate-reducing bacteria. Sources of data on potential mercury deposits associated with mining activity include USGS, the U.S. Bureau of Mines (for a list of major deposits of gold and silver), the State Inactive Mine Inventory, and the EPA Superfund program. Examples of TMDLs involving mercury associated with mining are provided in appendix E.

Sediments. A TMDL analysis should account for any mercury present in sediments as a result of current and past mercury loadings. Mercury in sediments may be the result of past metals mining activity as described above, past industrial activity, and historical air deposition. Data on levels of mercury in sediments are important in determining which sources are most significant, the most appropriate approach for addressing the sources and how long it will take to achieve water quality standards. For example, development of appropriate allocations, and in turn development of management strategies, may need to address both current sources of deposition as well as legacy sources. An examination of past industrial practices in the watershed could include whether sediments might serve as a reservoir for mercury. Various national databases, such as the National Sediments Database (USEPA 2002g) and data collected by USGS might help to identify isolated locations of elevated mercury in sediments. EPA has also developed a detailed guide on sediment source analysis in the first edition of *Protocol for Developing Sediment TMDLs*: http://www.epa.gov/owow/tmdl/sediment/pdf/sediment.pdf.

In the absence of sediment data for a waterbody, site-specific monitoring might be needed to confirm the levels of mercury in sediments to use as input to water quality models. In the sediment TMDL for Bellingham Bay, Washington, site-specific sediment analyses for mercury and other pollutants were conducted, including sediment sampling and toxicity analyses. Two kinds of modeling were also conducted:

- Modeling of contaminant transport and mixing to determine whether loadings from a location were contributing to water quality standards violations
- Screening modeling to identify other potential sources of sediment contamination (see the TMDL at http://www.epa.gov/waters/tmdldocs/1991_Bellingham%20Bay%20TMDL.pdf)

Other examples of TMDLs involving an analysis of mercury contributions from sediments include the TMDLs for Pena Blanca, Arizona, and the Cache Creek watershed in California (see appendix D). As described in the section on allocations, the Cache Creek watershed TMDL also accounts for methylmercury production in sediments.

Natural or background levels of mercury in soils. Soils and sediments can include mercury of geologic origin or mercury produced by the weathering of geologic materials, together with mercury of anthropogenic origin (mercury emitted over time from human sources and then deposited on soils). Mercury in soils can also re-emit or become re-suspended and subsequently redeposit to soils. Local studies have been used in some TMDLs to estimate the geologic contributions of mercury to waterbodies. For example, a TMDL developed for the Ouachita watershed in Arkansas relied on a study of mercury concentrations in the rocks of the Ouachita Mountains (FTN 2002). The mercury concentration estimated to be of geologic origin was then subtracted from the total concentration of mercury measured in soils to estimate the nongeologic concentration of mercury in soils.

6.2.2.2 What modeling tools are available to link mercury sources and water quality?

When developing a TMDL, states and authorized tribes should characterize the association between the concentration of methylmercury in fish tissue and the identified sources of mercury in a watershed. The association is defined as the cause-and-effect relationship between the selected targets, in this case the fish tissue-based criterion and the sources. The association provides the basis for estimating the total assimilative capacity of the waterbody and any needed load reductions. TMDLs for mercury typically link models of atmospheric deposition, watershed loading, and mercury cycling with bioaccumulation. For example, a watershed model (e.g., Grid Based Watershed Mercury Model, GBMM) might be linked with a receiving water mercury model (e.g., Water Quality Analysis Simulation Program, WASP) and a bioaccumulation model (e.g., Bioaccumulation and Aquatic Simulator, BASS). These models are described further in appendix E. Linking models together can enable a translation between the endpoint for the TMDL (expressed as a fish tissue concentration of methylmercury) and the mercury loads to the water without having explicit water column criteria or translations. The analysis determines the loading capacity as a mercury loading rate consistent with meeting the endpoint fish tissue concentration. This section describes some of the modeling tools available for use in mercury TMDLs.

When selecting a model or models for developing a mercury TMDL, states and authorized tribes should first consider whether the models will effectively simulate the management action(s) under consideration. If a percent reduction in mercury load to the waterbody is the sole action considered, a simple model might suffice; to answer more complex questions, a more complex or detailed model might be needed. Some questions decision makers should address include:

- How much do specific mercury loads need to be reduced to meet the criterion?
- What are the relative sources of the mercury load to the segment?

- Are mercury loads to the waterbody from sediments and watershed runoff and concentrations in fish at equilibrium with respect to current deposition levels? If not, how much will an equilibrium assumption affect the accuracy of predicted future fish concentrations?
- Could other pollution-control activities reduce mercury loads to the waterbody or affect the mercury bioaccumulation rate?
- After regulatory controls are implemented, how long will it take for fish tissue levels to meet the criterion?

Depending on the types of questions states and authorized tribes ask and the management approaches they consider, appropriate models could range from a very simple steady state model to a comprehensive dynamic simulation model, as described below. In addition, models are often used in TMDL analyses but are not required. For more information on the specific models described here, see http://www.epa.gov/athens and http://www.epa.gov/crem.

6.2.2.2.1 Steady state models and the proportionality approach

Steady state modeling describes the dynamic equilibrium between environmental media established in response to constant loads over the long term. Consequently, complex mercury cycling processes can be compressed into simple equations. One such approach, assumes that a ratio of current to future fish tissue concentration equals the ratio of current to future mercury loads to the waterbody. This approach, often referred to as the proportionality approach and explained in detail in the Mercury Maps report (USEPA 2001b), assumes that where air deposition is the sole significant source, factors affecting methylation remain unchanged. As a result, the ratio of current to future fish tissue concentrations can be assumed to equal the ratio of current to future air deposition loads in this situation. Mercury Maps, and the situations in which the proportionality assumption may or may not apply, are described further in appendix E.

A number of mercury TMDLs where air deposition is the predominant mercury source have been developed using an assumption of proportionality between mercury deposition and fish tissue methylmercury concentration. Specifically, such TMDLs have reasoned that a reduction in deposition will result in a proportional reduction in mercury concentrations in fish over time. Such an approach applies to situations where air deposition is the only significant mercury source and relies on steady-state conditions. This approach may also be used to estimate the reductions needed to meet a fish tissue target without necessarily calculating a water column target.

Mercury TMDLs which applied a proportional relationship between reductions in deposition and reductions in fish tissue methylmercury concentration include TMDLs for waterbodies in Louisiana, such as the Ouachita Basin (FTN 2002), the Mermentau and Vermillion-Teche River Basins (USEPA 2001i, 2001j) and the Coastal Bays and Gulf Waters of Louisiana (Parsons 2005). Using the Everglades Mercury Cycling Model, the pilot mercury TMDL study in the Florida Everglades also reported a linear relationship between mercury deposition and the concentrations of mercury in largemouth bass (Atkeson et al. 2002).

More recently, the Minnesota statewide mercury TMDL applied the proportionality approach. As described in section 6.2.1 above, waterbodies within the state were grouped into two regions, and a TMDL developed for each region. Minnesota calculated a reduction factor for each region, or the percent reduction in total mercury load needed in each region to achieve the fish tissue target of 0.2 mg/kg for the 90th percentile of the standard-length fish (MPCA 2007). Using the proportionality assumption, Minnesota applied the regional reduction factor (51 percent for the southwest region and 65 percent for the northeast region) to the total source loadings to determine the load reduction goal. The Minnesota TMDL explains in further detail the basis for using the proportionality approach.

Mass balance models are somewhat more complex implementations of the steady state approach. In place of a simple ratio, such models describe fluxes of mercury in and out of the model domain (e.g., impaired segment) and, optionally, balance fluxes (e.g., methylation and demethylation) within the model domain. The advantage provided by this approach is that individual fate processes can also be simulated. For example, if soil erosion and sediment runoff are modeled, decreased mercury soil erosion load can be related to decreased fish tissue concentrations (AZDEQ 1999). Where all other aspects of a watershed and waterbody remain unchanged, steady state models can produce as accurate an estimate of the necessary load reductions as a dynamic model, generally with less-intensive data collection and analysis. In addition, such simple approaches might be less prone to calculation error and are much easier for the public to understand.

6.2.2.2.2 Continuous-simulation and dynamic models

Continuous-simulation and dynamic models take into account time-varying effects such as variable pollutant inputs, precipitation, hydrologic responses, seasonal ecosystem changes, and effects on fish tissue concentrations. For mercury, they might also include a variety of physical and chemical fate and transport processes such as oxidation, demethylation, volatilization, sedimentation, resuspension, and adsorption and desorption. Dynamic models can be important in establishing cause-and-effect relationships. They assemble available scientific knowledge on mercury fate and transport into a single picture. Such models have been used to demonstrate how mercury moves from air emission to deposition to watershed runoff to subsequent bioaccumulation in fish at observed levels in remote waterbodies (USEPA 1997c).

Dynamic models could be used to describe waterbodies in dis-equilibrium (e.g., a recent surface water impoundment with elevated methylation rates). The Everglades Mercury TMDL pilot project (USEPA 2000g) simulated the amount of time necessary to attain equilibrium in response to reduced mercury loads using the Everglades Mercury Cycling Model. The model results predicted that sediments would continue to supply as much as 5 percent of the mercury load 100 years after air deposition reductions occurred. The Dynamic Mercury Cycling Model (D-MCM) was used in the mercury TMDLs for McPhee and Narraguinnep reservoirs in Colorado and the TMDLs for Arivaca and Pena Blanca lakes in Arizona (see appendix D) (Tetra Tech 2001).

The SERAFM model incorporates more recent advances in scientific understanding and implements an updated set of the IEM-2M solids and mercury fate algorithms described in the 1997 *Mercury Study Report to Congress* (USEPA 1997c).

Dynamic models can also describe how fish tissue concentrations are expected to respond to environmental variability, such as seasonal or year-to-year changes in meteorology. Thus, they can be used to better interpret how samples collected in a specific season of a specific year would be expected to vary relative to other seasons or years with mercury loads being constant.

6.2.2.2.3 Spatially detailed models

Spatially detailed models, such as that used in the Savannah River mercury TMDL (USEPA 2001j), can demonstrate how mercury fish tissue concentrations are expected to vary with distance downstream of the impaired segment(s). For the Savannah River, EPA used the Water Quality Analysis Simulation Program (WASP) model. WASP is a dynamic, mass balance framework for modeling contaminant fate and transport in surface water systems. The model helps users interpret and predict water quality responses to natural phenomena and man-made pollution for various pollution management decisions. Another model that has been used for mercury TMDLs is the EPA Region 4 Watershed Characterization System (WCS). WCS is a geographic information system (GIS)-based modeling system for calculating soil particle transport and pollutant fate in watersheds (Greenfield et al. 2002).

As with the steady state mass balance model, including additional processes can allow a modeler to determine the impact of different environmental regulatory or management controls on mercury fish tissue concentrations. For example, where mercury transport to a waterbody occurs predominantly through soil erosion, erosion control might be identified as a useful nonpoint source control on mercury to waterbodies (Balogh et al. 1998). As another example, controls on acid deposition and, thus, changes in lake pH and their effect on fish tissue mercury concentrations can also be modeled (Gilmour and Henry 1991, Hrabik and Watras 2002). Finally, spatially detailed landscape models hypothetically could be used to reflect the local effects of wetlands and their impacts on mercury methylation rates.

6.2.2.2.4 Regression models

In general, a regression model is a statistical model describing how a parameter, such as mercury levels in fish, is related to one or more variables. Regression models provide only approximations of real trends.

One example of a regression model for mercury is the regression-based model under development for New England. The model, known as MERGANSER (Mercury Geospatial Assessments for the New England Region), is being developed by EPA and several partners. The partners include USGS, the Biodiversity Research Institute, the State of Vermont, the Clean Air Association of the Northeast States, and the New England Interstate Water Pollution Control Commission. The model will integrate recent atmospheric mercury-deposition models with many databases on mercury sources, mercury levels in fish and bird tissue, and ecosystem features that might be associated with the risk of mercury contamination in biota and, ultimately, humans.

The intent of the project is to identify, by using regression modeling, explanatory variables that contribute to elevated mercury levels in fish and wildlife in New England. The model can then be applied in a predictive mode to lakes throughout New England

that have no mercury fish tissue or loon blood data. Specifically, the model will (1) identify watershed and other factors associated with high mercury levels in fish and wildlife; (2) identify likely sources of mercury; (3) provide estimates of mercury levels in fish and wildlife at any lake or stream in New England; (4) provide estimates of mercury reductions needed from air deposition to meet water-quality criteria; and (5) identify optimal locations for long-term monitoring. Modeling will be done within a GIS environment so that the spatial distribution of data is retained and results can be displayed watershed by watershed. Maps from MERGANSER will show the areas in New England that are susceptible to high mercury levels in biota and that are, therefore, areas where human health impacts (through fish consumption) and ecological impacts (bird tissue mercury levels) are potentially occurring. In addition, the model can be used to produce maps that identify mercury sources and show the relative magnitude of mercury loading from those sources.

6.2.2.2.5 Model selection

When selecting a model, a state or authorized tribe should be aware of the assumptions inherent in each type of model and consider the potential effects of those assumptions on relationships between loadings and fish tissue levels or water quality. The first consideration for model assumptions is methylation. Several factors, including pH, redox, potential sulfate concentrations, temperature, dissolved organic carbon (DOC) concentrations, salinity, and microbial populations, influence the speciation of mercury (Ullrich et al. 2001). If these factors fluctuate seasonally around an average condition, a waterbody could be at a dynamic equilibrium and the steady state assumption would still apply over the long term. If these factors change over time such that they might have a significant impact on fish tissue concentrations, the equilibrium assumptions inherent in steady state modeling might not hold, and a dynamic model like the D-MCM (EPRI 1999) should be used. In using this model, the state or authorized tribe should consider the amount of environmental media concentration data needed to initialize the model to represent its non-equilibrium state.

The second consideration for model assumptions is the BAF. As discussed in section 3.1.3.1, the BAF assumes a constant proportionality between fish tissue methylmercury concentrations, water column methylmercury concentrations, and water column mercury concentrations. Mercury in a waterbody might not be at a steady state because of ongoing reductions in mercury emissions, changes in water chemistry that affect methylation, changes in aquatic ecosystem makeup, or changes in fish biomass. If these factors change with time, the equilibrium assumptions inherent in steady state modeling might not hold, and a dynamic model should be used.

The third consideration for model assumptions is the relative importance of the mercury in aquatic sediments to the concentrations in fish tissue. Depending on previous loadings to the watershed, the deposition pattern of solids, and the chemistry in the aquatic sediments, the mercury in sediments can significantly influence the mercury concentrations in fish tissue. Sediments are repositories, and the loading that caused sediment mercury could be a legacy source. If so, a simplified steady state approach cannot simulate changes in mercury concentrations in fish tissue due to external loading reductions, and a dynamic model should be used.

6.2.2.2.6 Model limitations

To effectively estimate fish methylmercury concentrations in an ecosystem, it is important to understand that the behavior of mercury in aquatic ecosystems is a complex function of the chemistry, biology, and physical dynamics of different ecosystems. The majority (95 to 97 percent) of the mercury that enters lakes, rivers, and estuaries from direct atmospheric deposition is in an inorganic form (Lin and Pehkonen 1999). Microbes convert a small fraction of the pool of inorganic mercury in the water and sediments of these ecosystems into methylmercury. Methylmercury is the only form of mercury that biomagnifies in organisms (Bloom 1992). Ecosystem-specific factors that affect both the bioavailability of inorganic mercury to methylating microbes (e.g., sulfate, DOC) and the activity of the microbes themselves (e.g., temperature, organic carbon, redox status) determine the rate of methylmercury production and subsequent accumulation in fish (Benoit et al. 2003). The extent of methylmercury bioaccumulation is also affected by the number of trophic levels in the food web (e.g., piscivorous fish populations) because methylmercury biomagnifies as large piscivorous fish eat smaller organisms (Watras and Bloom 1992; Wren and MacCrimmon 1986). These and other factors can result in considerable variability in fish methylmercury levels among ecosystems at the regional and local scales.

The lack of complete knowledge about key mercury process variables, such as the functional form of equations used to quantify methylation rate constants, is a major contributor to overall uncertainty in models that cannot be quantified at this time.

6.2.2.3 What are the allocation approaches in mercury TMDLs?

A requirement for an approvable TMDL is that the state or authorized tribe allocate the pollutant load necessary to achieve water quality standards among point and nonpoint sources. EPA's regulations, however, leave the decision regarding how to allocate loadings to the state or authorized tribe developing the TMDL. States and authorized tribes have discretion in selecting a method or system for allocating pollutant loads among sources, provided that the allocations will result in attainment of water quality standards represented by the loading capacity (40 CFR 130.2). States and authorized tribes could reasonably consider the relative contribution of each source as one factor in developing allocations. Other factors might include cost-effectiveness, technical and programmatic feasibility, previous experience with the approach being considered, likelihood of implementation, and past commitments to load reductions. These same considerations apply to mercury TMDLs.

A number of pollutant loading and allocation scenarios have occurred in mercury TMDLs, each with a different mix of point and nonpoint sources. The scenarios have ranged from situations where mercury loadings are predominantly from air deposition, with small loadings from point sources or other sources, to situations where mercury loadings are predominantly from past mining activity. In addition, allocation approaches in mercury TMDLs have included allocations to individual sources as well as allocations to sectors and regions where appropriate. Examples of scenarios involving different source mixes and allocation approaches in approved mercury TMDLs are provided below.

Mercury loadings predominantly from air deposition, with very small loadings from point sources or other sources

Contributions from air deposition, such as direct deposition to the waterbody and deposition to the watershed transported to the waterbody by runoff and erosion, are typically included as part of the load allocation. As discussed in EPA guidance on reviewing TMDLs, allocations for nonpoint sources may range from reasonably accurate estimates to gross allotments (USEPA 2002f). TMDLs where air deposition is the predominant mercury source have usually allocated only a small portion of the reductions to the point sources or wasteload allocation, as described in the examples below. Many mercury TMDLs have included an allocation to air deposition as a whole; in some mercury TMDLs, the contributions from air deposition are further allocated to within-state and out-of-state sources, and contributions from anthropogenic and natural contributions are distinguished.

The Savannah River mercury TMDL is one of the first examples of an approach to allocating loadings where the predominant mercury source is atmospheric deposition. Many of the TMDLs developed to date are for situations where air deposition is the predominant mercury source. The Savannah River mercury TMDL indicated that NPDES point sources contribute 1 percent of the mercury loadings, while atmospheric deposition contributes 99 percent of the loadings. The TMDL identified only one point source on the Georgia side of the river that has a permit to discharge mercury to the Savannah River. It identified 28 point sources in Georgia that might have the potential to discharge larger amounts of mercury in their effluent according to the nature of the discharge or the mercury levels that have been found in their effluents above the water quality standard level.

The Savannah River mercury TMDL assigned 99 percent of the load reductions to the air sources and 1 percent of the reductions to point sources. The TMDL provides specific wasteload allocations for these 28 sources on the basis of meeting the water quality criterion at the end of a pipe or, alternatively, implementing a pollutant minimization program. In addition, the TMDL identifies about 50 other point sources expected, on the basis of their size and nature, to discharge mercury at levels below the water quality standard or not add mercury in concentrations above the concentrations in their intake water. Individual wasteload allocations are given to these point sources on the basis of their holding their effluents at current levels. The wasteload allocations for these point sources are expressed in the TMDL as a sum or aggregate allocation.

Note: After the Savannah River mercury TMDL was issued, Georgia adopted a new interpretation of its narrative water quality criteria that used EPA's new recommended fish tissue criterion for methylmercury. On the basis of the new interpretation, Georgia determined, and EPA agreed, that the Savannah River was meeting water quality standards for mercury. EPA therefore withdrew the TMDL. EPA believes, however, that the decisions, policies, and interpretations set forth in the TMDL are still valid and provide an example of a possible approach to mercury TMDLs. The Savannah River mercury TMDL is at http://www.gaepd.org/Files_PDF/techguide/wpb/TMDL/Savannah/EPA_Savannah_River_Watershed_Hg_TMDL.pdf.

The series of mercury TMDLs issued February 28, 2002, for watersheds in middle and south Georgia, such as the Ochlockonee watershed, also illustrate the first scenario. In

these basins, point source loadings contribute very little to the mercury loadings (the cumulative loading of mercury from all point sources is less than 1 percent of the total estimated current loading), with the vast majority of loading to the basins as air deposition.

The Ochlockonee mercury TMDL assigns most of the load reductions to the air sources, with a load allocation of 1.16 kg/yr and a wasteload allocation of 0.06 kg/yr. Although point sources collectively contribute a very minute share of the mercury load, the Ochlockonee and other mercury TMDLs for middle and south Georgia include wasteload allocations for the point sources. The TMDLs include wasteload allocations for each facility identified as a significant discharger of mercury, with the remainder of the allocation assigned collectively to the remaining point sources, considering that these smaller point sources would reduce their mercury loadings using appropriate, cost-effective minimization measures. The TMDL was written so that all NPDES-permitted facilities would achieve the wasteload allocation through discharging mercury at concentrations below the applicable water quality standard or through implementing a pollutant minimization program. A summary of the Ochlockonee mercury TMDL is provided in appendix D and is at http://gaepd.org/Files_PDF/techguide/wpb/TMDL/Ochlockonee/EPA_Ochlockonee_River_Hg_TMDL.pdf.

The Minnesota "statewide" mercury TMDL document takes a regional approach to allocations, providing a single wasteload allocation and a single load allocation that applies to each region rather than to individual waterbodies. The TMDL document indicates that such a regional allocation serves as a regional "cap." The predominant source is atmospheric deposition, with a small contribution (about 1.2 percent of the total source load for both regions combined) from point sources. The wasteload allocation is set at 1 percent of the TMDL or the 1990 baseline load, whichever is lower, with the remainder allocated to nonpoint sources. Point sources, including NPDES-permitted stormwater sources, municipal treatment facilities, and industrial dischargers that impact the waterbodies covered by the TMDL, are subject to the wasteload allocation. For the load allocation, the Minnesota TMDL estimates the contributions to air deposition from within-state and out-of state sources, as well as from global sources and anthropogenic sources. A summary of the Minnesota mercury TMDL is included in appendix D. The TMDL and related documents can be found at http://www.pca.state.mn.us/water/tmdl/tmdl-mercuryplan.html.

Mercury loadings predominantly from past mining activity, with small or no contributions from atmospheric deposition and/or NPDES point source contributions

One example of a TMDL for this scenario is the Cache Creek Watershed TMDL. Cache Creek is a tributary to the Sacramento-San Joaquin Delta in California. Sources of mercury entering the Cache Creek watershed include leaching from waste rock and tailings from historical mercury and gold mines, erosion of naturally mercury-enriched soils, geothermal springs, and atmospheric deposition. There are multiple inactive mercury and gold mines in the Cache Creek watershed and no NPDES-permitted discharges. Methylmercury is also produced *in situ* in the streambed of Cache Creek. The TMDL analysis provides load allocations for Cache Creek, as well as each of the tributaries. For each waterbody, load reductions are provided for both methylmercury and total mercury. Allocations are expressed as a percentage of the existing methylmercury

loads. Estimated atmospheric contributions of mercury, from direct deposition and runoff after deposition, are very small compared to loads of mercury from mine sites or erosion of the stream bed and banks, and thus no allocations are made to air deposition. Reducing the methylmercury loads will require a multifaceted approach that includes controlling inorganic mercury loads and limiting the entry of inorganic mercury into sites with high rates of methylmercury production. The Cache Creek watershed mercury TMDL and the allocation approach are summarized further in appendix D.

Mercury loadings from a combination of different sources, including atmospheric deposition, past mining, and point sources

The Mercury TMDL for the Willamette Basin, Oregon, identifies atmospheric deposition (direct plus indirect deposition: 47.7 percent) and erosion of mercury-containing soils (47.8 percent) as the top sources, along with small contributions from legacy mining (0.6 percent) and NPDES-permitted point sources (3.9 percent). The point source loadings consist of 2.7 percent from POTWs and 1.2 percent from industrial discharges. The TMDL assigns interim allocations to each of the source categories or sectors, rather than individual sources, based on the considerable uncertainty in the loading estimates and other factors. The TMDL specifies an across-the-board reduction of 27 percent in each source. After the 27 percent reduction to each source, the allocations for the Willamette mainstem are approximately similar to their relative contribution to the total loadings: 44.7 kg/yr for air deposition, 44.8 kg/yr for erosion, 0.6 kg/yr for legacy mine discharges, 2.6 kg/yr for POTWs, 1.1 kg/yr for industrial discharges, and 0.8 kg/yr for reserved capacity. Allocations are also provided for other waterbodies in the basin. The TMDL is at http://www.deq.state.or.us/wq/tmdls/docs/willamettebasin/willamette/chpt3mercury.pdf.

Mercury loadings from point sources predominate or are not insignificant compared to other sources

A small number of approved TMDLs have been developed for situations where mercury is primarily or exclusively from point sources, including TMDLs for waterbodies in Colorado. Examples of such TMDLs can be found at http://iaspub.epa.gov/tmdl_waters10/attains_impaired_waters.control?p_state=CO&p_pollutant_id=693.

6.2.2.4 What kinds of monitoring provisions have been associated with approved TMDLs?

Monitoring provisions in approved TMDLs have included point source effluent and influent monitoring, as well as water column, fish tissue, sediment, and air deposition monitoring. Examples of mercury TMDLs with post-TMDL monitoring are the middle and south Georgia mercury TMDLs approved in 2002. For facilities with the potential to discharge significant amounts of mercury on the basis of their large flow volume or other factors, the TMDL provides the permitting authority with two options for the wasteload allocation:

- Implement the criteria-end-of-pipe (i.e., apply the TMDL water quality target to a discharger's effluent at the outfall point).
- Monitor for mercury in the facilities' influent and effluent using more sensitive analytical techniques (e.g., EPA method 1631) and implement cost-effective mercury minimization if mercury is present in effluent at concentrations greater

than source water concentrations and if the discharge exceeds the water quality target.

Other facilities expected to discharge at levels below the water quality target will be expected to verify through monitoring whether or not they are significant dischargers of mercury. Other follow-up activities include further characterization of the air sources and additional ambient monitoring of mercury concentrations in water, sediment, and fish.

The mercury TMDL for the coastal bays and gulf waters of Louisiana (approved July 2005) includes similar monitoring provisions for point source dischargers with flows above a specified discharge volume. The TMDL also indicates that Louisiana will conduct water, fish tissue, and air deposition monitoring and that the state will develop a statewide mercury risk reduction program, including an assessment of all mercury sources. (See the TMDL and supporting documents at http://iaspub.epa.gov/tmdl/waters_list.tmdl_report?p_tmdl_id=11642.)

TMDLs involving past mining activity have also included follow-up monitoring; examples include three of the TMDLs described in appendix D (Clear Lake, California; Arivaca Lake, Arizona; and Cache Creek, California). The mercury TMDL for Arivaca Lake lists several follow-up actions and monitoring activities, such as additional watershed investigations to identify other potential mine-related mercury sources, including sediment sampling; evaluation of livestock BMPs to reduce erosion of soils containing mercury and follow-up monitoring; and fish tissue monitoring to evaluate progress toward the TMDL target (see the TMDL at http://www.epa.gov/waters/tmdldocs/17.pdf). The Clear Lake, California, mercury TMDL also identifies the need for follow-up monitoring of fish tissue and sediment (see appendix D, and the TMDL at http://www.swrcb.ca.gov/rwqcb5/water_issues/tmdl/central_valley_projects/clear_lake_hg/cl_final_tmdl.pdf. The Cache Creek TMDL indicates that monitoring will be conducted to determine whether mercury loads have been reduced and to measure progress toward the TMDL target, as well as to better characterize areas of methylmercury production and mercury loadings from tributaries. Monitoring will include fish tissue, sediment, and water monitoring.

EPA recommends that states and authorized tribes periodically review TMDLs during implementation to ensure that progress is being made toward achieving water quality standards. Such “adaptive implementation” provides the flexibility to refine and improve a TMDL as data on the success of implementation activities are collected. States may refine information on the contributions from sources such as runoff from abandoned mining sites, sediment loading of mercury-laden sediments, and air deposition as data and modeling tools improve. States should consider the application of adaptive implementation in determining load allocations for these sources. Although a monitoring plan is not required in a TMDL, EPA guidance documents recommend using a monitoring plan to track the effectiveness of a TMDL; see *Guidance for Water Quality-Based Decisions: the TMDL Process* (EPA 440/4-91-001). Post-TMDL monitoring is an important tool for evaluating implementation success and, if necessary, refining the TMDL. Follow-up monitoring may include monitoring of water quality, fish tissue, air deposition, and sediments.

7 National Pollutant Discharge Elimination System (NPDES) Implementation Procedures

7.1 What are the general considerations in NPDES permitting?

Section 301(a) of the CWA prohibits the discharge of any pollutant, including mercury, from a point source into waters of the United States except in compliance with certain enumerated provisions of the CWA, among them section 402. CWA section 402 establishes the NPDES program, under which EPA or states and tribes authorized to administer the program issue permits that allow the discharge of pollutants into waters of the United States, notwithstanding the general prohibition established by section 301(a). These permits must contain (1) technology-based effluent limitations, which represent the degree of control that can be achieved by point sources using various levels of pollution control technology (see CWA sections 301, 304, and 306) and (2) more stringent limitations, commonly known as water quality-based effluent limitations (WQBELs), when necessary to ensure that the receiving waters achieve applicable water quality standards (see CWA section 301(b)(1)(C)).[20]

Most WQBELs are expressed as numeric limits on the amounts of specified pollutants that may be discharged. However, WQBELs may also be expressed in narrative form such as best management practices (BMPs) or pollutant minimization measures (e.g., practices or procedures that a facility follows to reduce pollutants to waters of the United States) when it is infeasible to calculate a numeric limit (see 40 CFR 122.44(k)(3)). In addition, BMPs may be imposed in the form of NPDES permit conditions to supplement numeric effluent limitations when the permitting authority determines that such requirements are necessary to carry out the purposes and intent of the CWA (see CWA section 402(a)(1)(B) and 40 CFR 122.44(k)(4)).

As noted above, NPDES permits must contain WQBELs when necessary to achieve applicable water quality standards. The procedure for determining the need for WQBELs is called a "reasonable potential" analysis. Under EPA's regulations at 40 CFR 122.44(d)(1)(i), effluent limitations must control all pollutants that the permitting authority determines "are or may be discharged at a level that will cause, have the reasonable potential to cause, or contribute to an exceedance of any applicable water quality standard." Thus, if a pollutant discharge has the reasonable potential to cause or contribute to an exceedance of applicable water quality standards, the discharger's NPDES permit must contain a WQBEL for that pollutant (see 40 CFR 122.44(d)(1)(iii)–(vi)). The procedure for determining reasonable potential must consider the variability of the pollutant in the effluent, other loading sources, and dilution (when allowed by the water quality standards) (see 40 CFR 122.44(d)(1)(ii)). The procedure specifies only

[20] When developing WQBELs, the permitting authority must ensure that the level of water quality achieved by such limits derives from and complies with water quality standards (see 40 CFR 122.44(d)(1)(vii)(A)).

whether a discharge must have a WQBEL; it does not specify the actual permit limits. The NPDES regulations at 40 CFR 122.44(d)(1)(vii) specify that the level of water quality to be achieved by the WQBEL must derive from and comply with water quality standards, as required by CWA section 301(b)(1)(C) (requiring "any more stringent limitation… necessary to meet water quality standards"). This would necessarily be a permit-by-permit determination.

7.2 What is the EPA-recommended NPDES permitting approach for methylmercury?

The recommendations below assume that an approved TMDL is not available at the time of permit issuance. If EPA has approved or established a TMDL containing wasteload allocations for the discharge of mercury (and methylmercury where appropriate), the WQBEL for that discharge must be consistent with the wasteload allocation (see 40 CFR 122.44(d)(1)(vii)(B)).

EPA believes, depending on the particular facts, that a permit writer may reasonably conclude that limits on point sources consistent with this guidance are likely to be as stringent as necessary to achieve water quality standards. As described in more detail below, the permit writer should conduct a reasonable potential analysis to determine whether a discharger will cause or contribute to the exceedance of applicable water quality standards. Once such a determination is made, limits can be imposed consistent with this guidance. In circumstances where waters are not yet impaired, the permit writer should consider other factors or conditions when determining whether a facility has reasonable potential with the goal of preventing future impairments. (See Sections 7.2.2, 7.5.1.2.2 and 7.5.1.2.3).

7.2.1 Developing NPDES permit limits based on the fish tissue criterion

The first component of the recommended NPDES permitting approach for methylmercury is to determine how the methylmercury criterion is expressed in the applicable water quality standard and to determine whether a water column translation of the fish tissue criterion or site-specific data to translate are available at the time of permit issuance. This will inform the selection of the appropriate recommended implementation option. If the methylmercury criterion is expressed as a water column value, the permit writer should develop permit limits based on this criterion according to procedures described in section 5.4.4 of the *Technical Support Document for Water Quality-based Toxics Control*, or TSD (USEPA 1991). If the criterion is expressed as a fish tissue value and a water column translation of the fish tissue criterion or site-specific data to translate are available at the time of permit issuance, the permit limits based on the translated water concentration value should again be developed according to procedures described in section 5.4.4 of the TSD.

If, however, the criterion is expressed as a fish tissue value and a water column translation of the fish tissue criterion or site-specific data to translate are not available at the time of permit issuance, the permitting authority may reasonably conclude that a numeric WQBEL is infeasible to calculate. In that instance, EPA recommends that the permitting authority develop NPDES permit limits based on the criterion using the

procedures described below. Section 7.3 contains additional information about expressing and developing permit limits based on the methylmercury criterion.

7.2.2 Determining reasonable potential

The second component of the recommended NPDES permitting approach for methylmercury is to conduct a reasonable potential analysis to determine whether the discharge will cause or contribute to an exceedance of applicable water quality standards. The recommended reasonable potential analysis consists of two steps. Step one is to determine whether there is a quantifiable amount of mercury in the discharge using a sufficiently sensitive analytical method (see sections 7.4 and 7.5.1.1 for more information on sufficiently sensitive methods.) If this information is unknown, EPA recommends including a monitoring requirement in the permit to collect this information and a reopener clause to allow establishment of appropriate requirements if the permitting authority determines that the discharge has reasonable potential. If, using a sufficiently sensitive analytical method, there is not a quantifiable amount of mercury in the discharge, depending on the particular facts, the permitting authority may reasonably conclude that the discharge does not have reasonable potential and that no water quality-based limits are necessary. If there is a quantifiable amount of mercury, however, the permitting authority should move to step two of the reasonable potential analysis. Section 7.5.1.1 contains additional information on step one of the reasonable potential analysis.

Step two of the reasonable potential analysis is to determine whether the fish tissue concentration of methylmercury in the receiving water is close to or exceeds the criterion.

If the fish tissue concentration of methylmercury in the receiving water is below and not close to the criterion, depending on the particular facts, the permitting authority may reasonably conclude that the discharge does not have reasonable potential, but tier 2 antidegradation provisions should be considered. This situation is described below in the third component of the NPDES permitting approach.

If the fish tissue concentration of methylmercury in the receiving water is close to or exceeds the criterion, depending on the particular facts, the permitting authority may reasonably conclude that the discharger has reasonable potential, and a WQBEL must be included in the permit. Recommended WQBELs for this situation are described below in the fourth component of the NPDES permitting approach. Section 7.5.1.2 contains additional information on step two of the reasonable potential analysis. If information for step two is unknown, EPA recommends including in the permit a special permit condition to conduct a fish tissue survey of the receiving waterbody and a reopener clause so that reasonable potential can be determined when the fish tissue data become available. EPA further recommends that in this situation the permitting authority encourage permittees to develop and implement mercury minimization plans (MMPs) to reduce mercury loading to the waterbody.

In order to prevent future impairments, EPA recommends that a state or authorized tribe consider other factors or conditions such as rising fish tissue concentrations or the relative contribution of mercury or methylmercury from the source when determining whether a facility has reasonable potential in waters that are not yet impaired. Section

7.5.1.2.2 contains additional examples of other factors, such as downstream impacts, that should be considered in a reasonable potential analysis.

7.2.3 Implementing antidegradation

The third component of the recommended NPDES permitting approach for methylmercury is to determine whether the discharger will undertake an activity that can increase mercury loading to the waterbody. If the discharger will not undertake such an activity, no additional permit conditions are necessary. EPA recommends, however, that in this situation the facility voluntarily develop and implement an MMP to reduce the facility's mercury loading to the receiving water. If the discharger will undertake such an activity, EPA recommends that a tier 2 antidegradation analysis be conducted in accordance with the state or tribe's antidegradation policy and that permit conditions consistent with the analysis be included in the permit.

As part of conducting a tier 2 antidegradation analysis, the state or authorized tribe would evaluate the activity's potential to lower water quality, whether there are alternatives that would avoid lowering water quality, and whether lowering of water quality would be necessary to accommodate important economic or social development in the area of the discharge. EPA considers analyses of potential pollution prevention and enhanced treatment alternatives as an appropriate starting point for the antidegradation review for both industrial and municipal dischargers. See 67 FR 68971, 68979. The results of such an analysis of potential alternatives could provide the basis for developing an MMP.

EPA further recommends that the permit contain a special condition requiring the permittee to implement an MMP and conduct effluent monitoring to allow for evaluation of the effectiveness and implementation of the MMP. Section 7.5.1.2.2 contains additional information on antidegradation considerations.

7.2.4 Establishing appropriate WQBELs

The fourth component of the recommended NPDES permitting approach for methylmercury is to develop appropriate WQBEL requirements. Where a TMDL containing wasteload allocations for the discharge of mercury (and methylmercury where appropriate) has been developed, the WQBEL for that discharge must be consistent with the wasteload allocation (see 40 CFR 122.44(d)(1)(vii)(B)). Where a TMDL is not available at the time of permit issuance, to satisfy 122.44(d)(1)(vii)(A), EPA recommends the following WQBEL requirements, which are explained in greater detail in section 7.5.2.1:

- Where a water column translation of the fish tissue criterion has been developed, or where site-specific data to do so are readily available, include a numeric water quality-based limit.
- Where a water column translation or site-specific data are not available and the permit writer determines that a numeric limit is infeasible to calculate:
    - Require the permittee to implement an MMP tailored to the facility's potential to discharge mercury. Depending on the particular facts, the permitting authority may include in the MMP a trigger level, reduction goal, or

enforceable numeric level (e.g., existing effluent quality) to further manage mercury discharges.

- Require effluent monitoring using a sufficiently sensitive EPA-approved method to enable evaluation of the effectiveness and implementation of the MMP. (See sections 7.4 and 7.5.1.1 for more information on sufficiently sensitive methods.)
- Include a reopener clause to modify the permit conditions if the MMP is not found to be effective or if a water column translation of the fish tissue criterion is developed.

Since permitting authorities need to establish and maintain WQBELs as stringent as necessary to meet water quality standards, if a state or tribe has yet to complete the transition from an existing water column criterion to a fish tissue-based criterion, states may consider retaining their existing water column criteria until translators are developed. Alternatively, until a translator is available, EPA recommends that one of the approaches outlined in this document for relating a concentration of methylmercury in fish tissue to a concentration of methylmercury in ambient water be considered, especially for waters with relatively high direct water inputs of mercury. (See section 3.1.3.1.)

In modifying or reissuing permits with existing WQBELs for mercury, permit writers must also ensure compliance with CWA anti-backsliding requirements. As described elsewhere in this Guidance, CWA section 402(o)(1) prohibits the revision of WQBELs to make them less stringent than existing permit limits unless a specific exception applies under 402(o)(2) or 303(d)(4).

Exceptions under Section 402(o)(2), which would allow for the establishment of less stringent limits are:

(1) There have been material and substantial alterations or additions to the permitted facility which justify the less stringent limit.

(2) New information (other than revised regulations, guidance, or test methods) is available that was not available at the time of permit issuance, and that would have justified a less stringent limit.

(3) Good cause exists due to events beyond the permittee's control (e.g., natural disasters) and for which there is no reasonably available remedy.

(4) The permit has been modified under 301(c), 301(g), 301(h), 310(i), 301(k), 301(n), or 316(a).

CWA section 303(d)(4) provides additional exceptions to the anti-backsliding prohibition: paragraph (A), which applies to "non-attainment waters," and paragraph (B), which applies to "attainment waters".

- **Non-attainment water:** CWA section 303(d)(4)(A) allows the establishment of a less stringent effluent limitation when the receiving water does not meet applicable water quality standards (i.e., a "non-attainment water") if the permittee meets two conditions. First, the existing effluent limitation must have been based on a total maximum daily load (TMDL) or other wasteload allocation established under

CWA section 303. Second, relaxation of the effluent limitation is allowed only if the cumulative effect of all revised limitations would assure the attainment of water quality standards, or the designated use not being attained is removed in accordance with the water quality standards regulations.

- **Attainment water:** CWA section 303(d)(4)(B) applies to waters where the water quality equals or exceeds levels necessary to protect the designated use, or to otherwise meet applicable water quality standards (i.e., an "attainment water"). Under CWA section 303(d)(4)(B), a limitation based on a TMDL, wasteload allocation, other water quality standard, or any other permitting standard may only be relaxed where the action is consistent with the state's antidegradation policy.

The application of these exceptions is limited under 402(o)(3), which prohibits the relaxation of effluent limitations in all cases if a revised effluent limitation would result in a violation of applicable effluent limitation guidelines or water quality standards, including antidegradation requirements.

In establishing WQBELs for mercury, permit writers will need to ensure that the CWA anti-backsliding requirements are met. The first step of the inquiry is to determine whether the WQBEL based on the fish tissue criterion is "less stringent" than the WQBEL in the previous permit. If the new permit limit is not less stringent (e.g., if the prior numeric WQBEL is included in the MMP as an enforceable numeric level (see section 7.5.2.4 for additional information)), then the anti-backsliding prohibition should not be triggered and it should be appropriate to include the new limit in the permit. If the WQBEL based on the new fish tissue criterion is in fact less stringent than the prior WQBEL, then the permit writer must retain the existing numeric WQBEL unless there is an available exception to the anti-backsliding prohibition.

Because CWA section 402(o)(2)(B)(i) does not allow backsliding solely because regulations are revised (e.g., adoption of the fish tissue criterion), any applicable exceptions to the anti-backsliding prohibition for impaired waters would be found under section 303(d)(4)(A). In this case, permit limits based on TMDLs or other wasteload allocations established under section 303 can be made less stringent only if: a) the cumulative effect of all loadings meets the WQS or b) the designated use is removed.

Anti-backsliding requirements are further described in EPA's *NPDES Permit Writers' Manual* (USEPA 1996a) and in EPA's *Technical Support Document for Water Quality-Based Toxics Control* (USEPA 1991).

Other considerations and requirements may be necessary in developing permits. They include the following:

- Where a discharger undertakes an activity that could increase mercury loading to the receiving water, the WQBEL must be consistent with applicable antidegradation requirements (see section 7.5.1.2.2). Additional requirements may also be necessary under the CWA and EPA's NPDES regulations (see section 7.5.2.3).

- The permitting authority would need to include appropriate technology-based limits pursuant to CWA section 301(b) and 40 CFR sections 125.3 and 122.44(a)(1) (see section 7.5.2.3).

The entire recommended NPDES permitting approach is summarized in figure 5 and explained in greater detail in the following sections.

7.3 How does EPA recommend implementing the fish tissue criterion for NPDES permits?

As discussed in section 3.1, states and authorized tribes that decide to use the recommended criterion as the basis for new or revised methylmercury water quality standards have the option of adopting the criterion into their water quality standards as a fish tissue concentration, a traditional water column concentration, or both. If states or authorized tribes choose to use both approaches, they should clearly describe in their standards how each will be used for specific applications and describe applicable implementation procedures.

EPA recommends two approaches for implementing the fish tissue-based methylmercury water quality criterion in NPDES permits, depending on the form in which the state or authorized tribe expresses the criterion—as a fish tissue concentration or as a water column concentration. In addition, states and authorized tribes that adopt the recommended criterion as a fish tissue value may choose to implement it through NPDES permitting as a water column translation of the fish tissue value. Each of these approaches is summarized in figure 6 and discussed in more detail in sections 7.4 and 7.5.

The recommendations below assume that an approved TMDL is not available. If EPA has approved or established a TMDL containing a wasteload allocation for the discharge of mercury (and methylmercury where appropriate), the WQBEL for that discharge must be consistent with the wasteload allocation (see 40 CFR 122.44(d)(1)(vii)(B)).

This chapter provides EPA's guidance on how a permitting authority could implement the fish tissue criterion in NPDES permits consistent with the CWA and its implementing regulations. States and authorized tribes retain the discretion to develop and use procedures for determining reasonable potential and establishing effluent limits in NPDES permits that differ from those in the guidance. Such procedures may use other information relevant to determining reasonable potential and establishing effluent limits, where appropriate. If a state or authorized tribe develops its own such permitting procedures, EPA recommends that states and authorized tribes make the procedures public so that all stakeholders can be aware of the requirements and expectations of the permit program. In addition, the permit's fact sheet or statement of basis should also explain the basis of the permit conditions and effluent limitations and how these are consistent with the state's or authorized tribes' permitting procedures, the CWA, and applicable federal regulations.

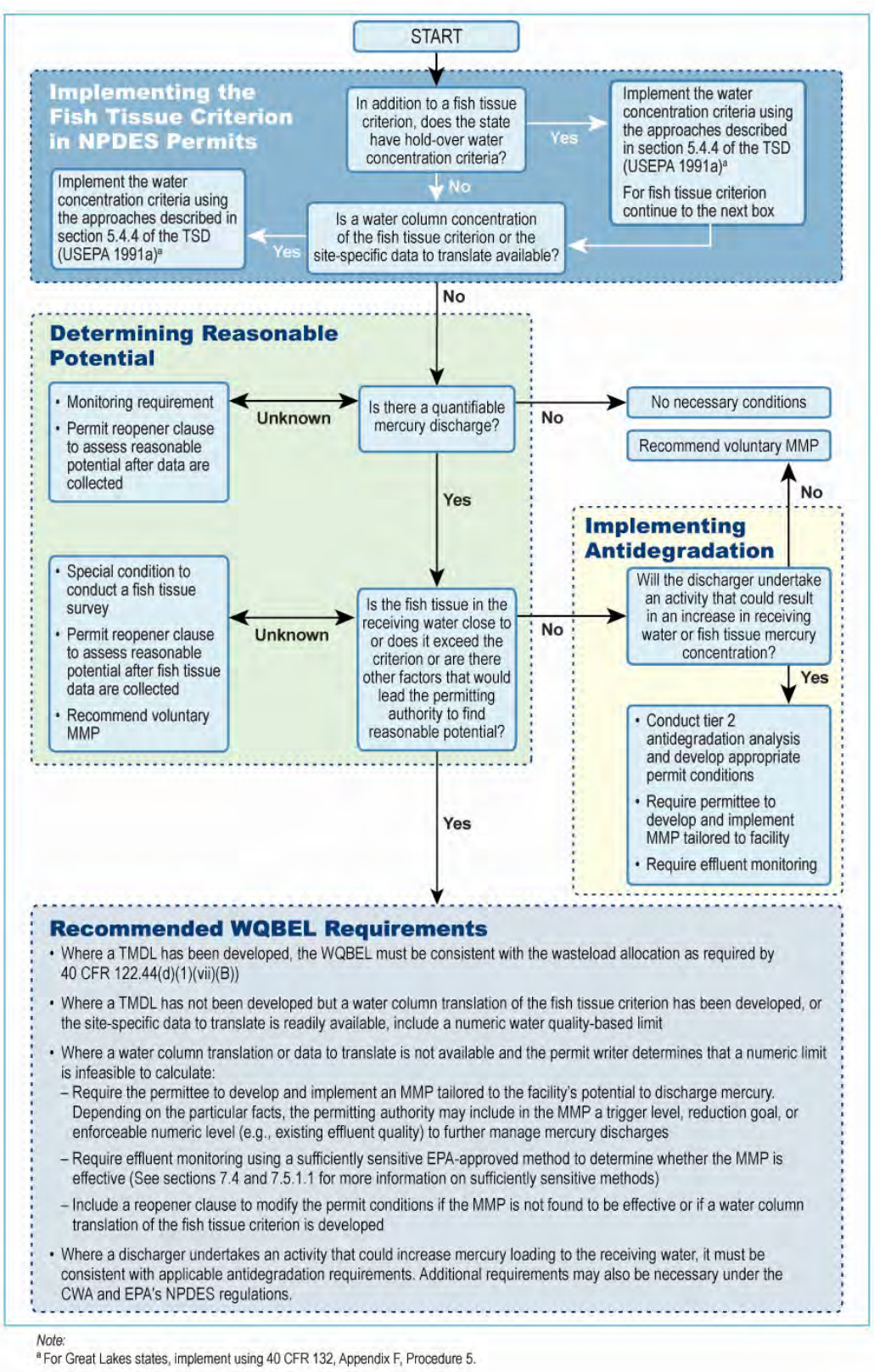


Figure 5. NPDES permitting approach for methylmercury.

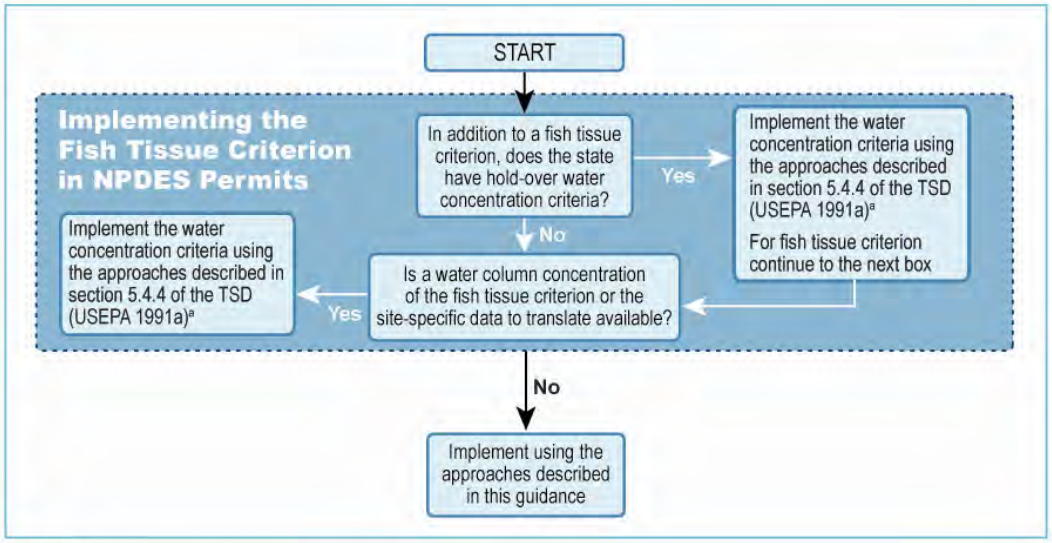


Figure 6. Implementing the fish tissue criterion in NPDES permits.

7.4 What are the procedures for developing permit limits when the criterion is adopted as a water column value or when the criterion is adopted as a fish tissue value and the permitting authority uses a water column translation of the fish tissue value?

This approach assumes that a state or authorized tribe decides to adopt a new or revised water quality criterion for methylmercury in one of the following forms:

- *Water column concentration value*. Expressing a criterion as a water column value is very common, and permitting authorities have considerable historical experience in developing permit limits based on such criteria in NPDES permits.

- *Fish tissue concentration value that is translated into a water column value*. Sections 3.1.3.1 through 3.1.3.3 of this guidance discuss the procedures for translating the fish tissue criterion into a water column value for water quality standards purposes. These procedures may also be used to translate a fish tissue criterion into a water column value for determining reasonable potential and for deriving numeric WQBELs.

In either case described above, the permitting authority should determine reasonable potential and calculate numeric WQBELs using the procedures described in section 5.4.4 of the TSD (USEPA 1991) to derive a numeric WQBEL.

This approach relies on the measurement of mercury in effluent, often at concentrations below the quantitation levels of some analytical methods. Therefore, the permitting authority should specify that the NPDES regulated discharger use a sufficiently sensitive EPA-approved method for the measurement of mercury in the discharge. An analytical method is sufficiently sensitive when (1) its method quantitation level is at or below the

level of the applicable water quality criterion or (2) its method quantitation level is above the applicable water quality criterion, but the amount of mercury in a discharge is high enough that the method detects and quantifies the level of mercury in the discharge. To illustrate the latter, if the water column criterion or water column translation of a fish tissue criterion for mercury in a particular waterbody is 2.0 parts per trillion (ppt), method 245.7 (with a quantitation level of 5.0 ppt) would be sufficiently sensitive when it reveals that the level of mercury in a discharge is 5.0 ppt or greater. In contrast, method 245.7 would not be sufficiently sensitive when it resulted in a level of nondetection for that discharge because it could not be known whether mercury existed in the discharge at a level between 2.0 and 5.0 ppt (less than the quantitation level but exceeding the water quality criterion).[21]

The selection of a sufficiently sensitive method relates method quantitation levels to the water column criterion value. If a water column criterion or a water column translation of a fish tissue criterion is not available to allow for selecting an alternate sufficiently sensitive method, EPA recommends the use of the most recent version of method 1631 to characterize discharges from all facilities for which the mercury levels are unknown or undetected. Method 1631 is relatively new, and the facilities may not have used it to analyze their effluent discharges. As a result, previous monitoring may show undetectable levels of mercury when use of method 1631 shows detectable or quantifiable amounts. Therefore, EPA recommends monitoring using the most recent version of method 1631 to help identify all facilities that contribute to mercury water quality impairment, unless another EPA-approved method can be justified as being sufficiently sensitive.

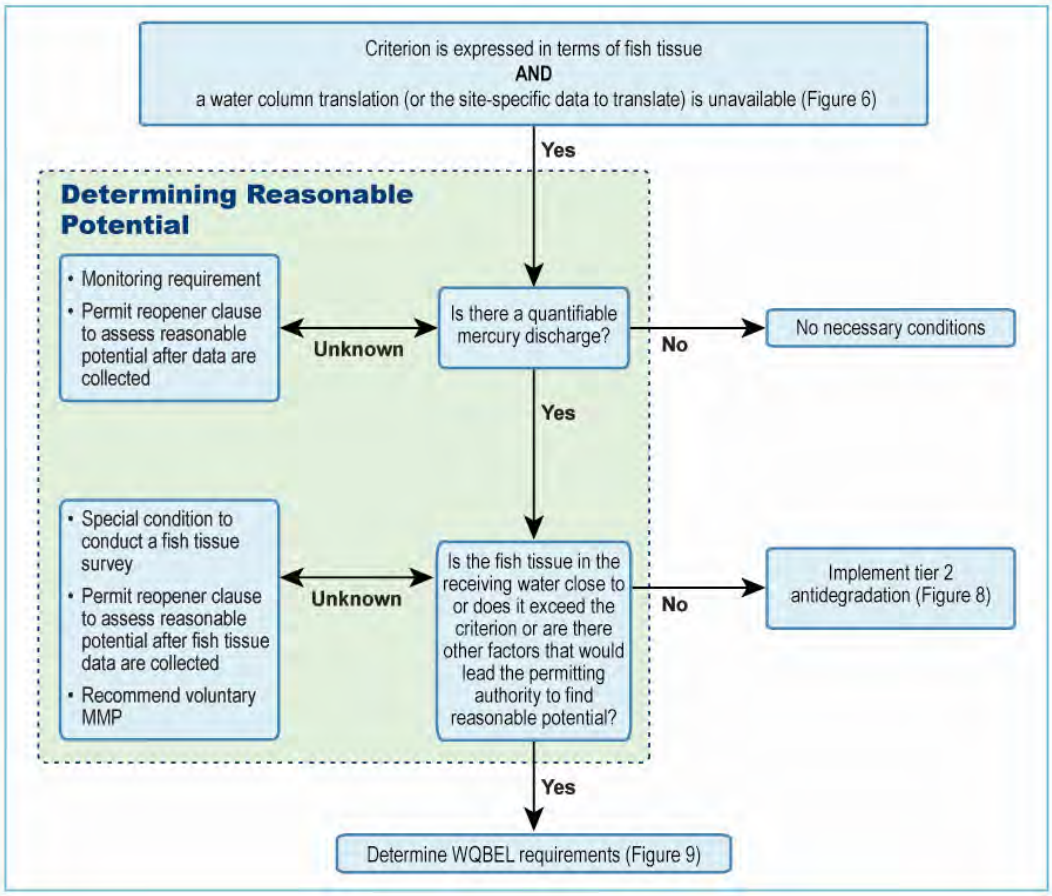
EPA's regulations require that measurements included on NPDES permit applications and on reports required to be submitted under the permit must generally be made using analytical methods approved by EPA under 40 CFR part 136. Because EPA has approved methods for analyzing mercury in water, these approved methods must be used in water analyses for NPDES permits involving mercury. See 40 CFR sections 122.21(g)(7), 122.41(j), 136.1, 136.3, and 136.6. Selection of an approved method should take into account the above discussion of method sensitivity. For metals, such as mercury, the federal regulations at 40 CFR 122.45(c) generally require effluent monitoring for the total form of the metal.

The discussion above describes analytical methods for measuring mercury in water. Refer to section 4.1 and appendix C for information on analytical methods for measuring mercury in fish tissue and for measuring methylmercury in water or fish tissue.

[21] For more information on choosing a sufficiently sensitive method, see the memorandum *Analytical Methods for Mercury in National Pollutant Discharge Elimination System (NPDES) Permits* from James A. Hanlon, Director of the Office of Wastewater Management, dated August 23, 2007, at http://www.epa.gov/npdes/pubs/mercurymemo_analyticalmethods.pdf.

7.5 What are the procedures for developing permit limits when the criterion is adopted as a fish tissue value and the permitting authority does not use a water column translation of the fish tissue value?

This approach assumes that a state or authorized tribe decides to adopt a new or revised water quality criterion for methylmercury in the form of a fish tissue concentration and that a TMDL, water column translation of the fish tissue criterion, or site-specific data to translate are not available at the time of permit issuance. As a result, the permitting authority will use a different approach than it has previously used for determining reasonable potential and expressing WQBELs. EPA recommends the approach described below, which is summarized in figure 7.



Note:
[a] For Great Lakes states, implement using 40 CFR 132, Appendix F, Procedure 5.

Figure 7. Determining reasonable potential.

7.5.1 How to determine the need for permit limits to control mercury (how to determine reasonable potential)

As discussed in section 3.1.2.2 of this document, EPA recommends that states and authorized tribes adopt new or revised methylmercury water quality criteria in the form of a fish tissue concentration. When a criterion is adopted into standards as a fish tissue value, states and authorized tribes may not have sufficient data to translate from a fish

tissue value to a traditional water column value using BAFs or translators. This section provides recommendations for how a permitting authority can determine reasonable potential in the absence of site-specific data to translate the fish tissue value into a water column value.

When determining reasonable potential, the permitting authority must determine whether the discharge "causes, has reasonable potential to cause, or contributes" to an exceedance of the applicable water quality criterion (see 40 CFR 122.44(d)(1)(ii)). The NPDES permit fact sheet should provide the rationale and assumptions used in determining whether WQBELs proposed in the associated draft permit are appropriate. The recommendations in this guidance could be applied on a permit-by-permit basis where appropriate to support the reasonable potential determination that satisfies 40 CFR 122.44(d)(1)(ii) with respect to a water quality criterion for methylmercury expressed as a fish tissue value in the absence of a TMDL and a water column translation of that value at the time of permit issuance.

EPA believes that, depending on the particular facts, a permitting authority could reasonably conclude that reasonable potential exists if two conditions are present: (1) the NPDES permitted discharger has mercury in its effluent at a quantifiable level and (2) the methylmercury level in fish tissue from the receiving waterbody is close to or exceeds the fish tissue water quality criterion. Under these circumstances, the effluent data indicate that the mercury load in the effluent contributes to the mercury load in the waterbody, and the fish tissue concentration indicates that the mercury load in the waterbody causes or has the potential to cause an exceedance of the water quality criterion. This approach is consistent with federal regulations pertaining to the Great Lakes Basin, which contained an approach for determining reasonable potential using fish tissue data (see 40 CFR part 132, appendix F, procedure 5.F.4). The reasonable potential approach for mercury described in this guidance has the advantage of significantly reducing environmental monitoring costs and does not involve developing a site-specific BAF for each waterbody in a state.

EPA recognizes that the mere presence of mercury at a quantifiable level in an effluent is not necessarily an indication that the mercury discharge is the sole cause of the fish contamination or even a substantial contributor of such contamination. However, mercury in an effluent discharge may contribute to the methylmercury present in fish tissue at levels close to or above the fish tissue criterion, and therefore the discharge may be found to exhibit the reasonable potential to cause or contribute to the exceedance of applicable water quality standards. EPA notes that the reasonable potential procedures as a whole are intended as conservative screening procedures to determine when a permit should contain a WQBEL to reduce the contribution to existing contamination or to prevent further possible degradation.

EPA notes that, unlike typical water quality criteria that are expressed as water column values, the fish tissue water quality criterion integrates spatial and temporal complexity and the cumulative effects of mercury loading from point and nonpoint sources that affect methylmercury bioaccumulation in aquatic systems. As discussed further in section 7.5.1.2.2, EPA believes that comparing the fish tissue concentration in steady state systems directly to the applicable fish tissue criterion appropriately accounts for the

factors specified in 40 CFR 122.44(d)(1)(ii) for a criterion expressed as a fish tissue value.

Finally, EPA further notes that because of the sensitivity of Method 1631E or other sufficiently sensitive methods (as described in section 7.4), it is reasonable to conclude that a discharge below quantitation does not have reasonable potential to exceed the criterion.

7.5.1.1 Step one of the reasonable potential analysis: Determining whether the NPDES-permitted discharger has mercury in its effluent at quantifiable levels

The first step in the reasonable potential analysis is to determine whether the discharge contains a quantifiable amount of mercury. To determine this, EPA recommends that permitting authorities require monitoring using a sufficiently sensitive analytical method approved for use by EPA under 40 CFR part 136. Section 7.4 contains additional information about sufficiently sensitive EPA-approved methods. If an alternate EPA-approved method cannot be justified as being sufficiently sensitive, EPA recommends monitoring using the most recent version of method 1631 to help identify all facilities that contribute to mercury water quality impairment. EPA recognizes that using method 1631 will likely result in a large majority of facilities showing quantifiable mercury discharges. This approach, however, is intended to allow permitting authorities to determine that facilities without quantifiable levels of mercury may not need step two of the reasonable potential analysis (determining whether the fish tissue criterion is being attained).

One of three outcomes will be reached in answering the first condition of the reasonable potential analysis:

- It is unknown whether the discharge includes a quantifiable amount of mercury.
- The discharge does not include a quantifiable amount of mercury.
- The discharge includes a quantifiable amount of mercury.

The recommended reasonable potential determination and recommended permit conditions for each of the outcomes is described in detail below.

7.5.1.1.1 What are the recommended permit conditions when it is unknown whether the discharge includes quantifiable amounts of mercury because there are limited or no effluent data to characterize the discharge of mercury?

In this situation, EPA recommends that the permitting authority include permit conditions that include the following elements:

- Effluent monitoring using a sufficiently sensitive EPA-approved analytical method to characterize the discharger's effluent for mercury (see sections 7.4 and 7.5.1.1 for information on sufficiently sensitive methods)
- A reopener clause to identify the actions that the permitting authority may take should the monitoring information indicate that a WQBEL for mercury is necessary

EPA recommends that permitting authorities require monitoring, using a sufficiently sensitive EPA-approved method, by all facilities for which the mercury levels are unknown or previously undetected (using less sensitive methods) to characterize the discharger's effluent for mercury. EPA recommends this monitoring to help identify all facilities that contribute to mercury loads in the waterbody. The permitting authority could obtain these monitoring data as part of the permit application, by requiring periodic (e.g., quarterly to annually) monitoring as part of the permit, or by invoking its authority under CWA section 308 (or equivalent state authority) to require NPDES facilities to collect information necessary for developing NPDES permit limits. The permit should include a reopener clause so that as soon as there is complete information and an indication that a more stringent limit is required, the permitting authority can establish the necessary requirements. The permitting authority may also decide to no longer require the monitoring if the information shows that the facility is not discharging mercury at quantifiable levels.

EPA recommends that when selecting the monitoring frequency, permitting authorities consider the factors in section 5.7.5 of the TSD (USEPA 1991). This section acknowledges that EPA has not recommended a specific monitoring frequency. However, the TSD recognizes that the choice of a monitoring frequency is a site-specific decision and provides the permitting authority with a number of factors to consider when making these decisions.

Until the permitting authority has sufficient data to determine whether the discharge has reasonable potential, and depending on the particular facts, the permit writer may reasonably conclude that the permit conditions described in this section are as stringent as necessary to achieve water quality standards, as required by CWA section 301(b)(1)(C).

7.5.1.1.2 What are the recommended permit conditions when the discharge does not include quantifiable amounts of mercury?

In this situation, EPA recommends that the permitting authority first review the monitoring data to determine whether they are representative of the effluent. If the permitting authority believes the monitoring data are representative of the discharge, no further permit conditions may be necessary. In contrast, if the permitting authority believes the data are not representative, the authority should consider requiring additional monitoring, as described in section 7.5.1.1.1.

7.5.1.1.3 What are the recommended actions for discharges that include quantifiable amounts of mercury?

In this case, the permitting authority should move to step two of the reasonable potential analysis and evaluate data on the concentrations of methylmercury in the fish tissue from the receiving waterbody to determine appropriate permit conditions (see section 7.5.1.2).

7.5.1.2 Step two of the reasonable potential analysis: Determining whether the fish tissue concentration of methylmercury in the receiving waterbody exceeds the fish tissue criterion

In step two of EPA's recommended fish tissue criterion reasonable potential procedure, the permitting authority has concluded that the first condition of the two-part reasonable potential analysis has been satisfied (i.e., the NPDES-permitted discharger has mercury in

its effluent at a quantifiable level). The permitting authority should then address the second condition of the reasonable potential analysis—determining whether the fish tissue from the receiving waterbody exceeds (or is close to exceeding) the fish tissue water quality criterion.

One of three outcomes will be reached in answering this question:

- The fish tissue concentration of methylmercury is unknown.
- The fish tissue concentration of methylmercury does not exceed the criterion or is not close to the criterion.
- The fish tissue concentration of methylmercury exceeds the criterion or is close to exceeding the criterion.

For discharges with quantifiable levels of mercury, the recommended reasonable potential determination and recommended permit conditions for each outcome is described in detail below.

EPA recognizes that when evaluating reasonable potential, the permitting authority should exercise discretion and careful judgment in determining whether fish tissue data are representative of current ambient conditions. EPA guidance for sampling strategies for fish tissue monitoring is provided in section 4.2 of this document.

7.5.1.2.1 What are the recommended permit conditions when a facility discharges quantifiable amounts of mercury but the fish tissue concentrations of methylmercury in the receiving waterbody are unknown?

In waterbodies for which there are insufficient fish tissue data available, a permitting authority cannot determine whether there is reasonable potential using a fish tissue approach. Therefore, in this case, EPA recommends that the permitting authority take the following actions:

- Include a special permit condition to conduct a mercury fish tissue survey for the receiving waterbody, unless such information will be available from another source in a timely manner.
- Include as a permit condition a reopener clause to identify the actions that the permitting authority may take should fish tissue monitoring information become available and indicate that a WQBEL for mercury is necessary.
- Encourage the permittee to develop and implement an MMP tailored to the facility's potential to discharge mercury.

In this instance, the permitting authority should start a process for collecting fish tissue data in the waterbodies where point source discharges of mercury exist. One approach for collecting this information is for the permitting authority to invoke its authority under CWA section 308 (state permitting authorities would use comparable state authorities) to require NPDES facilities to collect information necessary for the development of NPDES permit limits. In this case, the permitting authority could issue a section 308 letter or include special conditions in the permit to require the permittee to conduct a methylmercury fish tissue monitoring study. EPA recommends that the study design be

consistent with the recommendations on conducting ambient monitoring in section 4.2 of this guidance.

EPA also recommends that the permitting authority require only one study per waterbody. The permitting authority could do this by contacting all facilities that discharge into the waterbody and encouraging them to work jointly to conduct the study, because the outcomes of the study may affect the permit limits of those facilities. For example, the State of Idaho has developed a statewide fish tissue monitoring program for mercury that provides a standardized approach for collecting reliable data while recognizing limited resources for monitoring.

In waterbodies where the permitting authority expects to find high mercury concentrations in the water column or believes it will need a site-specific BAF to finish issuing the permits, the permitting authority should consider requiring the facility to include measurement of water column concentrations of mercury as part of the study.

EPA further recommends that the permit include a reopener clause so that as soon as there is complete information, the permitting authority can establish any additional requirements that are necessary. In this situation EPA recommends that the permitting authority encourage the permittee to develop and implement an MMP for the reasons discussed in section 7.5.1.2.2.1.

7.5.1.2.2 What are the recommended permit conditions when a facility discharges quantifiable amounts of mercury but the fish tissue concentrations of methylmercury in the receiving waterbody do not exceed and are not close to the criterion?

Once the permitting authority has determined that a facility discharges quantifiable amounts of mercury and that the concentration of methylmercury in fish tissue in the receiving waterbody does not exceed and is not close to the criterion, depending on the particular facts, the permitting authority may reasonably conclude that the discharge does not have reasonable potential to cause or contribute to an exceedance of the applicable fish tissue water quality criterion.

To assist in preventing future impairments, in some situations as outlined below, EPA recommends that states and authorized tribes also consider other factors or conditions such as a trend of rising fish tissue concentrations or the relative contribution of mercury or methylmercury from the source when determining whether a facility has reasonable potential in waters that are not yet impaired.

EPA notes that, unlike typical water quality criteria that are expressed as water column values, the fish tissue water quality criterion integrates spatial and temporal complexity as well as the cumulative effects of variable mercury loading from point and nonpoint sources that affect methylmercury bioaccumulation in aquatic systems. EPA believes that comparing the fish tissue concentration in steady state systems directly to the applicable criterion expressed as a fish tissue value appropriately accounts for the factors specified in 40 CFR 122.44(d)(1)(ii) for a criterion expressed as a fish tissue value. Existing tissue-based data are indicators of accumulation that has already occurred. Thus, where fish tissue concentrations in a watershed are expected to be constant (i.e., steady state conditions) or decreasing over time, data that indicate that the fish tissue criterion is

currently being attained may be effective indicators of current and potential continued future attainment.

However, in dynamic systems where the levels in tissue in a watershed may be expected to increase, EPA recommends that the permitting authority account for this as part of the reasonable potential determination that is designed to prevent potential future impairments.

Another factor that permitting authorities may consider is the impact of permitted discharges to downstream waters (e.g., a discharge to a river that flows into a lake where mercury is a concern). In such a circumstance, it may be appropriate to conclude that the discharge has reasonable potential on the grounds that its discharge causes or contributes to the excursion of the fish tissue criterion in the downstream water.

The presence of these other factors or conditions such as the relative contribution of mercury or methylmercury from the source, rising fish tissue concentrations, or potential excursion of the criterion downstream, could constitute a basis for concluding that an effluent limit is necessary depending on the particular facts.

As discussed in section 7.5.1.2.2.2, for discharges to waters that are not impaired, EPA recommends that states and tribes regard any activity that could result in an increase in receiving water or fish tissue mercury concentration as a significant lowering of water quality for the purposes of triggering an antidegradation review.

Implementing tier 2 antidegradation

If the facility undertakes any activity that could increase mercury loading to the receiving waterbody, an antidegradation review may be necessary. Such increases must be consistent with the applicable antidegradation policy. Federal regulations at 40 CFR 131.6 specify that tribal or state water quality standards must include an antidegradation policy, and federal regulations at 40 CFR 131.12 identify the elements of an acceptable antidegradation policy. Section 303(d)(4)(B) requires that applicable antidegradation requirements be satisfied prior to modifying NPDES permits (for example, prior to removing a WQBEL or including less stringent effluent limitations).

The federal antidegradation policy is composed of three levels of protection commonly referred to as tiers. The first tier, identified at 40 CFR 131.12(a)(1), protects the minimum level of water quality necessary to support existing uses and applies to all waters. This tier prohibits lowering water quality to the point where existing uses are impaired. The second tier, found at 40 CFR 131.12(a)(2), protects water quality where water quality is better than that needed to support “fishable/swimmable” uses of the water. Where these conditions exist, the waterbody is typically considered not impaired, and water quality must be maintained and protected unless it is demonstrated that lowering water quality is necessary to support important social and economic development and that existing uses will be fully protected. The third tier, at 40 CFR 131.12(a)(3), involves the protection of water quality in waterbodies that are of exceptional ecological, aesthetic, or recreational significance. Water quality in such waterbodies, identified and specifically designated by states or authorized tribes as Outstanding National Resource Waters, must be maintained and protected.

States and authorized tribes should determine whether the discharger will undertake an activity that can result in an increase in mercury loading to the receiving waterbody.

One of two outcomes will be reached in answering this question:

- The discharger will not undertake an activity that can increase mercury loading to the waterbody.
- The discharger will undertake an activity that can increase mercury loading to the waterbody.

As part of conducting a tier 2 antidegradation analysis, the permitting authority would evaluate the activity's potential to lower water quality, whether there are alternatives that would avoid lowering water quality, and whether lowering of water quality would be necessary to accommodate important economic or social development in the area of the discharge. EPA considers analyses of potential pollution prevention and enhanced treatment alternatives as an appropriate starting point for the antidegradation review for both industrial and municipal dischargers. See 67 FR 68971, 68979. The results of such an analysis of potential alternatives could provide the basis for developing an MMP.

EPA's recommendations for implementing antidegradation provisions and addressing increases in mercury loads are summarized in figure 8 and explained in sections 7.5.1.2.2.1 and 7.5.1.2.2.2. EPA recognizes, however, that states and tribes have the flexibility to interpret their antidegradation policies differently. For example, some states use limits established at existing effluent quality to implement their antidegradation provisions.

7.5.1.2.2.1 What are the recommended permit conditions when a facility discharges quantifiable amounts of mercury into a waterbody in which the fish tissue concentration of methylmercury does not exceed the criterion and the facility will not undertake an activity that could increase mercury loading to the waterbody?

If the facility discharges a quantifiable amount of mercury and the fish tissue concentration of methylmercury in the receiving water does not exceed the criterion, depending on the particular facts, the permitting authority may reasonably conclude that the discharge does not have reasonable potential to cause or contribute to an exceedance of the applicable fish tissue water quality criterion. In such situations, however, EPA recommends that the permitting authority encourage the facility to develop and implement an MMP.

An MMP helps ensure that the discharge will continue to have no reasonable potential to cause or contribute to an exceedance of applicable water quality standards. The recommendation to develop a voluntary MMP is also based on the extent of potential mercury impairment across the country and the scientific complexities of and uncertainties associated with assessing mercury loadings and evaluating their effects.

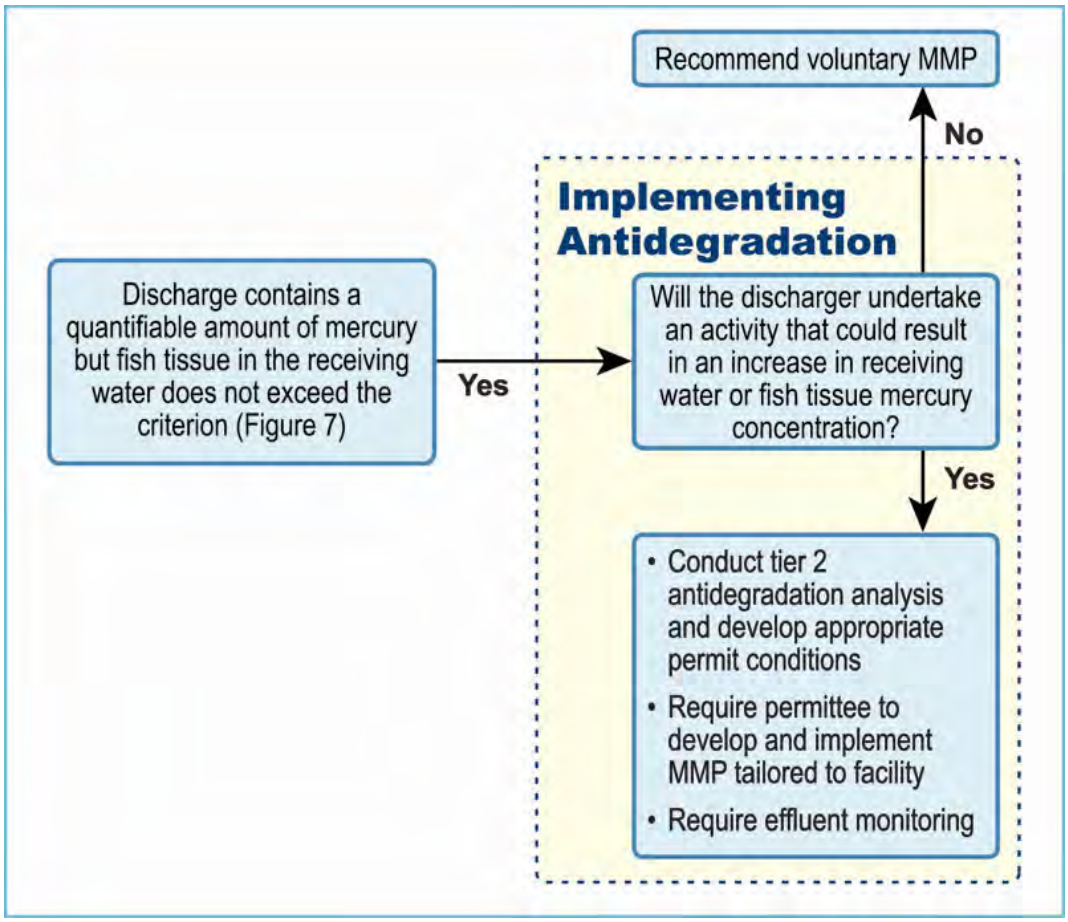


Figure 8. Implementing tier 2 antidegradation.

If future monitoring data demonstrate that a discharge does have reasonable potential, development of a MMP could assist the permit writer in establishing appropriate permit conditions. Furthermore, EPA believes that simply developing an MMP might provide dischargers of mercury with sufficient information to economically reduce the discharge of mercury into our Nation's waters by voluntarily implementing the mercury minimization measures identified in the plan. Section 7.5.2.1 provides additional information on MMPs.

7.5.1.2.2.2 What are the recommended permit conditions when a facility discharges quantifiable amounts of mercury into a waterbody in which the fish tissue concentration of methylmercury does not exceed the criterion but the facility will undertake an activity that could result in an increase in receiving water or fish tissue mercury concentration?

In this situation, the receiving water does not currently exceed the fish tissue criterion. EPA believes that increases in mercury loading to a waterbody should be allowed at levels determined appropriate by an antidegradation analysis and that such dischargers should be required to implement MMPs under the authority of CWA section 402(a)(1)(B) and 40 CFR 122.44(k)(4).

EPA recommends the following WQBEL requirements:

- Include permit conditions consistent with antidegradation requirements.
- Require the permittee to implement an MMP tailored to the facility's potential to discharge mercury. Depending on the particular facts, the permitting authority may include in the MMP a trigger level, reduction goal, or enforceable numeric level to further manage mercury discharges.
- Require the permittee to monitor its effluent using a sufficiently sensitive EPA-approved method (see sections 7.4 and 7.5.1.1 for information on sufficiently sensitive methods).

Other considerations and requirements might be necessary in developing permits:

- The permitting authority would need to include appropriate technology-based limits pursuant to CWA section 301(b) and 40 CFR sections 125.3 and 122.44(a)(1) .
- For modified or reissued permits with existing effluent limits for mercury, any less stringent effluent limit must be consistent with anti-backsliding requirements (see section 7.2.4).

Activities that would lower water quality in a high-quality water must be consistent with the applicable antidegradation provisions of a state's or authorized tribe's water quality standards. Consistent with EPA's antidegradation regulations for water quality standards, state and tribal antidegradation regulations are to provide that the quality of waters at levels better than the levels necessary to support "fishable/swimmable" uses of the water may be lowered only if the state or authorized tribe determines that allowing lower water quality is necessary to accommodate important economic or social development in the area in which the waters are located (see 40 CFR 131.12(a)(2)). EPA recommends that states and authorized tribes regard any activity that could result in an increase in receiving water or fish tissue mercury concentration as a significant lowering of water quality for the purposes of triggering a tier 2 antidegradation review. If the state's or authorized tribe's antidegradation analysis determines that the proposed lowering of water quality should not be allowed, the permitting authority would not authorize or allow any such discharge to occur. If the state's or authorized tribe's antidegradation analysis determines that a lowering of water quality is allowable, the level to which the discharger is ultimately allowed to lower water quality (on the basis of the applicable antidegradation requirements) would then be subject to a reasonable potential analysis. Also, EPA's antidegradation regulations for water quality standards require state and tribal antidegradation regulations to protect the minimum level of water quality necessary to support existing uses by prohibiting lowering of water quality to the point where existing uses are impaired (see 40 CFR 131.12(a)(1)).[22] For new and increased discharges, states have the flexibility to interpret their antidegradation policies differently. For example, some states use limits established at existing effluent quality.

[22] This part of the antidegradation analysis is similar to the reasonable potential determination and WQBEL development process that a permitting authority conducts for an existing discharger.

EPA expects that fluctuations in mercury loadings arising from normal industrial production fluctuations, or loading fluctuations that are not results of change in existing POTW service areas, would generally not trigger a tier 2 antidegradation analysis. EPA expects that increases in mercury loadings from a POTW arising from adding a new subdivision or an unsewered neighborhood to a sewer service area would generally trigger a tier 2 antidegradation review. If an antidegradation review is triggered, the review should consider the source of the increased mercury loading, the potential for source reduction through either treatment, pretreatment or pollution prevention, and the expected benefits likely to accrue to the affected community as a result of the activities that result in increased mercury loadings. EPA recommends that states and tribes tailor the level of detail and documentation for antidegradation demonstrations to the specific circumstances. For example, in some instances, as with diffuse domestic sources of mercury, available treatment and pollution prevention alternatives may be limited or lacking, leaving only the importance of social and/or economic development as the primary focus of the review.

EPA recognizes that an increase in the discharge of mercury might be due to mercury present in stormwater or input process water that does not originate with and is not under the reasonable control of a facility. While an MMP, to the extent that there are available BMPs to minimize mercury discharges, might still be appropriate in such circumstances, EPA would not generally expect that such discharges would trigger the need for an antidegradation review, or numeric WQBELs.

In addition to permit conditions consistent with antidegradation requirements, EPA recommends that the permit require the dischargers to implement an MMP under the authority of CWA section 402(a)(1)(B) and 40 CFR 122.44(k)(4). The MMP should be tailored to the individual facility's potential to discharge mercury. For more information on MMPs, see section 7.5.2.1.

7.5.1.2.3 What are the recommended permit conditions when a facility discharges quantifiable amounts of mercury and the fish tissue concentrations of methylmercury in the receiving waterbody are close to or exceed the criterion?

EPA believes that, depending on the particular facts, a permitting authority may reasonably conclude that reasonable potential exists if two conditions are present: (1) the NPDES-permitted discharger has mercury in its effluent at quantifiable levels, and (2) the fish tissue concentrations of methylmercury from the receiving waterbody are close to or exceed the fish tissue water quality criterion.

Where fish tissue concentrations are below but close to the criterion, EPA recommends that a finding of reasonable potential be made since the effect of current discharges and other relevant factors may not yet be reflected in fish tissue concentrations. For example, where the tissue data are below the water quality criterion, the permitting authority may consider applying an appropriate confidence interval (e.g., 95 percent upper confidence limit on the mean) to such values and compare that value to the fish tissue criterion to the extent necessary to account for variability in fish tissue data. As an example of an

alternative to this statistical approach, the State of Idaho's implementation guidance[23] for its methylmercury fish tissue criterion of 0.3 mg/kg recommends that where the levels in fish exceed 0.24 mg/kg, the permitting authority should determine that reasonable potential exists. Where methylmercury levels in fish tissue are thought to be relatively sensitive to a water point source load of mercury or methylmercury, the permitting authority may take that into account in the reasonable potential determination.

When reasonable potential exists, it is necessary to establish an appropriately protective WQBEL in the permit. For guidance on recommended WQBELs, see section 7.5.2.1.

7.5.1.3 How to consider mercury in intake water with a reasonable potential approach

For some facilities, the only source of mercury in a discharge may be the intake water taken directly from the same body of water to which the facility discharges. An example of this is a discharge of cooling water where the source of the cooling water is upstream of the discharge. In these situations where there are no known sources or additional contributions of mercury at the facility, the permitting authority could reasonably conclude, based on the particular facts, that there is no reasonable potential to cause or contribute to an exceedance of water quality standards. Furthermore, any slight increase in concentration after discharge (due to evaporation or other water loss) should not have an effect on the bioaccumulation of methylmercury in fish tissue unless the fish are known to frequently inhabit the water in the area immediately adjacent to the discharge. In making this decision, the permitting authority should consider the monitoring data from both the intake and discharge to verify that there are no known sources of additional contributions of mercury at the facility. EPA also recommends that permitting authorities consider evaluating whether the methylmercury concentration in fish tissue significantly increases for facilities with anaerobic conditions in the discharge. This procedure represents a comprehensive approach for conducting a site-specific analysis of the potential for a discharge to cause or contribute to an excursion above a water quality standard, which can lead to a decision to not require a WQBEL. This approach is consistent with the rationale for the federal regulations pertaining to the Great Lakes Basin, which included consideration of intake pollutants in finding reasonable potential (see 40 CFR part 132, appendix F, procedure 5.D).

7.5.2 Where reasonable potential exists, how can WQBELs be derived from a fish tissue value?

As discussed in section 3.1.2.2 of this document, EPA recommends that states and authorized tribes adopt a new or revised methylmercury water quality criterion in the form of a fish tissue concentration. When the criterion is adopted into standards as a fish tissue value, some states and authorized tribes may not have sufficient data to translate from a fish tissue value to a traditional water column value using BAFs or translators. When developing WQBELs, the permitting authority must ensure that the level of water quality to be achieved by such limits derives from and complies with water quality

[23] *Implementation Guidance for the Idaho Mercury Water Quality Criteria* is available at http://www.deq.state.id.us/water/data_reports/surface_water/monitoring/idaho_mercury_wq_guidance.pdf.

standards (see 40 CFR 122.44(d)(1)(vii)). This section provides recommendations on how a permitting authority could derive appropriate WQBELs in the absence of a TMDL and a water column translation of the fish tissue criterion at the time of permit issuance. The information discussed in this section is summarized in figure 9.

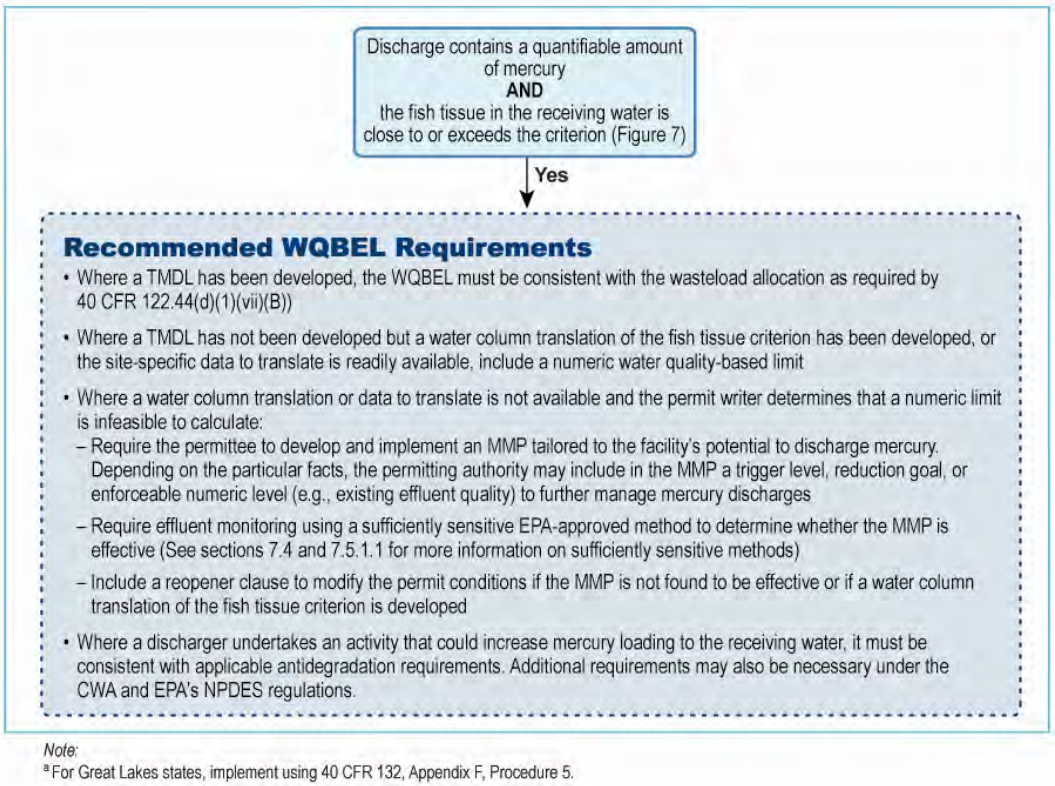


Figure 9. Determining WQBEL requirements.

7.5.2.1 What are the recommended WQBELs?

If the facility has a quantifiable amount of mercury in its discharge and the concentration of methylmercury in fish tissue in the receiving water is close to or exceeds the criterion, depending on the particular facts, the permitting authority may reasonably conclude that the discharge has reasonable potential to cause or contribute to an exceedance of the applicable fish tissue water quality criterion. In this situation, in the absence of a TMDL and a water column translation of the fish tissue criterion, it may be appropriate to conclude that it is infeasible to calculate a numeric WQBEL at the time of permit issuance and to instead express the WQBEL as narrative BMPs, as provided in 122.44(k)(3).

Where a TMDL containing wasteload allocations for the discharge of mercury (and methylmercury where appropriate) has been developed, the WQBEL for that discharge must be consistent with the wasteload allocation (see 40 CFR 122.44(d)(1)(vii)(B)). Where a TMDL is not available at the time of permit issuance, to satisfy 122.44(d)(1)(vii)(A), EPA recommends that the WQBEL consist of the following elements:

- Where a water column translation of the fish tissue criterion has been developed, or site-specific data to do so are readily available, include a numeric water quality-based limit.
- Where a water column translation or site-specific data are not available and the permit writer determines that a numeric limit is infeasible to calculate:
  - Require the permittee to implement an MMP tailored to the facility's potential to discharge mercury. Depending on the particular facts, the permitting authority may include in the MMP a trigger level, reduction goal, or enforceable numeric level to further manage mercury discharges.
  - Require effluent monitoring using a sufficiently sensitive EPA-approved method to enable evaluation of the effectiveness and implementation of the MMP. (See sections 7.4 and 7.5.1.1 for more information on sufficiently sensitive methods.)
  - Include a reopener clause to modify the permit conditions if the MMP is not found to be effective or if a water column translation of the fish tissue criterion is developed.

Other considerations and requirements may be necessary in developing permits:

- Where a discharger undertakes an activity that could increase mercury loading to the receiving water, it must be consistent with applicable antidegradation requirements. Additional requirements may also be necessary under the CWA and EPA's NPDES regulations.
- The permitting authority would need to include appropriate technology-based limits pursuant to CWA section 301(b) and 40 CFR sections 125.3 and 122.44(a)(1) .
- For modified or reissued permits with existing effluent limits for mercury, any less stringent effluent limit must be consistent with anti-backsliding requirements (see section 7.2.4).

7.5.2.2 What does EPA recommend where direct water inputs are relatively high?

This section describes EPA's recommendations where direct water inputs of mercury are relatively high. In this section, EPA discusses the recently developed "5m" listing approach for waters impaired by mercury from primarily atmospheric sources, as well as approaches for developing TMDLs, analyses of sources and loading capacity similar to what would be provided in a TMDL, or water column translations of the fish tissue criterion, to serve as the basis for permit limits.

As described in section 6.2, EPA recently developed an optional voluntary approach for deferring TMDL development for waters impaired by mercury predominantly from atmospheric sources pursuant to CWA section 303(d). Under this approach, states with comprehensive mercury reduction programs may consider waters appropriate for inclusion in a subcategory of their impaired waters lists (category 5m under the Integrated Report Guidance) and defer the development of TMDLs for those waters. EPA's 5m guidance states that in deciding on the scope of waterbodies proposed for

subcategory 5m, a contribution for states to consider would be approximately 90 to 95 percent of the loadings or higher from air deposition to the waterbody; the specific percent may vary, however. A full description of the 5m approach is at http://www.epa.gov/owow/tmdl/mercury5m/.

In watersheds where direct water inputs (mercury from point sources and nonpoint sources other than air deposition) represent a relatively high contribution of mercury, EPA recommends that states and authorized tribes specifically consider developing numeric permit limits for mercury dischargers to these waterbodies. States and authorized tribes may develop TMDLs for these waterbodies in the short term to provide important information for developing appropriate permit limits. Where a state or authorized tribe chooses not to develop a TMDL in the short term for such a waterbody, EPA recommends that the state or tribe develop an analysis of sources and loading capacity similar to what would be provided in a TMDL or a water column translation of the fish tissue criterion using the methods outlined in 3.1.3.1. Consistent with the 5m approach for establishing priorities for mercury TMDL development, in deciding whether there is a relatively high contribution from direct water inputs, a contribution for states to consider would be approximately 5 to 10 percent or more of mercury loadings from direct water inputs, taking into account that the specific percent may vary by state. At the same time, states may consider other factors, such as the complexity of the TMDL, in determining schedules for developing TMDLs.

Cumulative loads from point sources and localized nonpoint sources such as abandoned mines, contaminated sediments, and naturally occurring sources can potentially combine to cause localized mercury impairment. These situations are more complicated because the specific location and magnitude of each source could significantly affect fish tissue concentrations. In these situations, a TMDL provides the best basis for developing the appropriate permit limits.

Once EPA has approved or established a TMDL containing a wasteload allocation for the discharge of mercury (and methylmercury where appropriate), the permitting authority develops a WQBEL for a point source discharge that is consistent with the requirements and assumptions of the wasteload allocation in the TMDL (see 40 CFR 122.44(d)(1)(vii)(B)). In addition to developing a WQBEL, the permitting authority specifies monitoring requirements for the WQBEL (see 40 CFR 122.44(i) and 122.48). EPA recommends that permitting authorities require the permittee to use a sufficiently sensitive EPA-approved method for monitoring purposes.

In such watersheds where direct water inputs represent a relatively high mercury loading, EPA recommends that the permitting authority and the mercury dischargers in the watershed work together to collect the data necessary to develop a TMDL, an analysis of sources and loading capacity similar to what would be provided in a TMDL, or a water column translation of the fish tissue criterion. One approach for collecting information for a source analysis described above or a water column translation of the fish tissue criterion is for the permitting authority to invoke its authority under CWA section 308 (state permitting authorities would use comparable state authorities) to require NPDES facilities to collect information necessary for the development of NPDES permit limits. In the absence of a final TMDL, EPA recommends that a permitting authority conduct an analysis of sources and loading capacity similar to what would be provided in a TMDL.

Such an analysis that applied factors similar to those considered in a TMDL could be included in the fact sheet of the draft permit as a justification for the effluent limit being as stringent as necessary to attain the water quality standard. The permitting authority may also use a water column translation of the fish tissue criterion to derive numeric permit limits if such a translation or site-specific data to translate are available.

A water column translation of the fish tissue criterion may not always be necessary in developing a TMDL or an analysis of sources and loading capacity similar to what a TMDL would provide. For example, section 6.2.2.2.1 of this guidance provides descriptions of TMDLs that have been developed using steady state models and the proportionality approach.

Since permitting authorities need to establish and maintain WQBELs as stringent as necessary to meet water quality standards, if a state or tribe has yet to complete the transition from an existing water column criterion to a fish tissue-based criterion, states may consider retaining their existing water column criteria until translators are developed. Alternatively, until a translator is available, EPA recommends that one of the approaches outlined in this document for relating a concentration of methylmercury in fish tissue to a concentration of methylmercury in ambient water be considered (see section 3.1.3.1.)

7.5.2.3 What additional requirements may apply?

Activities that could increase mercury loadings to a receiving waterbody

Permits for sources that are seeking authorization to increase their discharge of mercury (or commence the discharge of mercury) must be consistent with applicable antidegradation requirements. See discussions of antidegradation elsewhere in this chapter, including sections 7.2.3 and 7.5.1.2.2.

The permitting authority may consider whether an offset of such discharges by other pollutant source reductions would support the development of a WQBEL that would ensure that the level of water quality to be achieved by such effluent limitation is derived from and complies with the water quality standards, as required by 40 CFR 122.44(d)(1)(vii)(A) and any other applicable NPDES regulations.

Pretreatment

A POTW is required to prohibit discharges from industrial users in amounts that result in or cause a violation of any requirement of the POTW's NPDES permit (see 40 CFR 403.2(a) and (b), 403.3(i) and 403.3(n)). A POTW that accepts mercury in its collection systems may need to ensure that its pretreatment program prevents its effluent from contributing to exceedance of the fish tissue criterion. The general pretreatment regulations (at 40 CFR part 403) require that each POTW, or combination of POTWs operated by the same water authority, with a design flow of 5.0 million gallons per day (MGD) or more develop an approved pretreatment program that protects against pass-through and interference, which may be caused by industrial discharges to the treatment facilities, by developing local limits for mercury and other pollutants or demonstrating that limits are not necessary for these pollutants. The POTW is also required to prohibit discharges from industrial users in amounts that result in or cause a violation of any requirement of the POTW's NPDES permit (see 403.2(a) and (b), 403.3(i) and 403.3(n)).

Federal categorical pretreatment standards, which are applicable to certain classes of industries, establish technology-based minimum pretreatment standards. The categorical standards, however, do not address POTW-specific problems that may arise from discharges by categorically regulated industries. In addition, many types of industries that discharge significant quantities of pollutants are not regulated by the categorical standards. Hence, there is a need for many POTWs to establish site-specific discharge limits to protect the treatment facilities, receiving water quality, and worker health and safety and to allow for the beneficial use of sludge.

Technology-based limits

When developing effluent limits for an NPDES permit, a permit writer must impose limits based on the technology available to treat mercury (technology-based limits) as a minimum level of control, as required by CWA section 301(b) and 40 CFR sections 125.3 and 122.44(a)(1). There are two general approaches for developing technology-based effluent limits for industrial facilities: national effluent limitation guidelines (ELGs) and best professional judgment (BPJ) on a case-by-case basis (in the absence of ELGs). Technology-based effluent limits for municipal facilities (POTWs) are derived from secondary treatment standards.

Anti-backsliding

Where a facility has a currently effective effluent limit for mercury and seeks a less stringent limit, the permitting authority must also comply with anti-backsliding requirements (see CWA section 402(o) and 40 CFR 122.44(l); see also CWA section 303(d)(4)). These requirements are described in EPA's *NPDES Permit Writers' Manual* (USEPA 1996b).

Permit documentation

Documentation is an important part of the permit development process. The NPDES permit fact sheet should provide an explanation of how the limit proposed in the associated draft permit is as stringent as necessary to achieve water quality standards (40 CFR 124.8 and 124.56). The recommendations in this guidance could be applied on a permit-by-permit basis, where appropriate, to support effluent limitations and other conditions that satisfy CWA section 301(b)(1)(C) and 40 CFR 122.44(d)(1) with respect to mercury.

7.5.2.4 Mercury minimization plans

EPA recommends that the permit contain a special condition requiring the permittee to implement an MMP that includes effluent monitoring using a sufficiently sensitive EPA-approved method (see sections 7.4 and 7.5.1.1 for information on sufficiently sensitive methods), with the expectation that effluent monitoring will allow for evaluation of the effectiveness and implementation of the plan. The MMP would be included in the permit in addition to a numeric WQBEL in cases where a TMDL, a water column translation of the fish tissue criterion, or other water concentration criterion is available at the time of issuance. If neither a TMDL nor a water column translation (or other water criterion) is available at the time of permit issuance, however, the MMP would be included in the permit as part of a narrative WQBEL in lieu of a numeric WQBEL. EPA believes that,

depending on the particular facts, a permit writer may reasonably conclude that such MMPs are as stringent as necessary to achieve water quality standards, for the reasons discussed below.

EPA believes that mercury reductions achieved through implementing MMPs tailored to the facility's potential to discharge mercury could result in important reductions in mercury loadings. EPA's basis for this conclusion is its study of pollutant minimization programs and their success in reducing mercury loadings to the environment. The reports *Mercury Study Report to Congress* (USEPA 1997c) and draft *Overview of P2 Approaches at POTWs* (USEPA 1999b) show that POTWs and industrial dischargers have implemented source controls, product substitution, process modification, and public education programs with great success. These minimization practices focus on sources and wastes that originate with and are under the reasonable control of a facility, not on pollutants in rainwater or source water.

As an example, POTWs can educate the public to prevent pollution by avoiding household products that contain high levels of mercury or substituting for those products ones that are mercury-free or more environmentally friendly. The most cost-effective approach for POTWs to substantially reduce mercury discharges appears to be pollution prevention and waste minimization programs that focus on high-concentration, high-volume discharges to the collection system, with considerable effort also directed at high-concentration, low-volume discharges such as those from medical and dental facilities.

Using pollutant minimization or prevention programs can also reduce the transfer from wastewater to other media through disposal of mercury-containing sludge from which mercury may subsequently reenter the environment. For example, mercury removed at a POTW through treatment is likely to reenter the environment through POTW sludges that are then incinerated or applied to land (although some is captured by air emission controls on incineration). EPA believes that a better approach for reducing mercury releases to the environment is to prevent mercury from entering the wastewater collection system at the source through product substitution, waste minimization or process modification, or removing and recycling mercury at the source (source controls) using state-of-the-art technology. These measures aimed at reducing influent loads to POTWs also reduce the use of mercury in the community, which could reduce the amount of mercury entering the environment through other media or sources. (For example, products that contain low levels of mercury may be disposed of as a nonhazardous solid waste and incinerated, releasing mercury to the air.) Where pollution prevention approaches have been implemented, substantial reductions in mercury concentrations in POTW influents, sludges, and effluents have been achieved. For a discussion of this approach, see the draft *Overview of P2 Approaches at POTWs* (USEPA 1999a). For an example of guidance on developing an MMP, see the EPA Region 5 final document *Mercury Pollutant Minimization Program Guidance*, dated November 2004 (http://www.epa.gov/region5/water/npdestek/mercury_pmp_nov_04_guidance.pdf). Many of the recommendations contained in the document are drawn from existing guidance and practice of state permitting authorities in EPA's Regional Office in Chicago. See also the City of Superior's document, *Mercury Pollutant Minimization Program Guidance Manual for Municipalities*, at http://www.ci.superior.wi.us/

index.asp?NID=129, and EPA's *Local Limits Development Guidance* (USEPA 2004) at http://www.epa.gov/npdes/pubs/final_local_limits_guidance.pdf.

Finally, as explained in section 2.1.1, mercury is a bioaccumulative, persistent pollutant that can cause adverse health effects. Given this fact, EPA believes that point sources that can cost-effectively reduce their mercury discharges should do so. The fact that air sources or historical contamination are likely dominant causes of impairment does not mean that point sources should not implement cost-effective, feasible pollution prevention measures to reduce their contribution of mercury to the environment, however small those contributions may be. In short, EPA believes that it is reasonable to expect NPDES permittees to implement cost-effective, feasible, and achievable measures to reduce the amount of mercury they discharge into the environment and that, depending on the particular facts, permit writers may reasonably conclude that permit limits that require such measures derive from and comply with water quality standards as required by EPA regulations at 40 CFR 122.44(d)(1)(vii)(A).

In cases where a permittee believes it may have reasonable potential, EPA recommends that the permittee provide information that the permitting authority can use in developing appropriate permit conditions and would encourage the permittee to provide a draft MMP. Alternatively, where a draft MMP is not initially submitted by the permittee, the permitting authority may request that the permittee provide a draft MMP. The permitting authority retains the final responsibility for determining reasonable potential, and for incorporating the appropriate permit conditions, including an effective MMP and its implementation, in the permit.

Developing an MMP need not be an intensive or burdensome activity. The content of an MMP should be determined on a case-by-case basis and tailored to the individual facility's potential to discharge mercury and implement reasonable controls. The MMP could be as little as one or two pages or as much as a major engineering study. Table 6 contains suggestions for the content of an MMP based on the type of facility. Of course, MMPs should vary in their level of detail and degree of stringency on the basis of site-specific factors and the degree to which the facility has the ability to reduce environmental releases of mercury. For example, if the mercury analysis performed for the permit application shows a much higher concentration than would be expected for the type of facility, further investigation would be appropriate and could lead to increased requirements. On the other hand, EPA recognizes that MMPs may not be effective in certain cases such as when an increase in the discharge of mercury may be due to the presence in stormwater or input process water that does not originate with and is not under the reasonable control of a facility.

If a permittee has several of the types of sources listed in table 6, each of these sources should be considered in developing an appropriate MMP. For example, if the service area of a POTW contains dental offices and medical facilities, the MMP should contain appropriate measures for both. The mercury minimization measures suggested in table 6 are expected to reduce mercury levels in the wastewater discharge as well as other waste streams and media. Most of the mercury discharged to POTWs, for example, ends up in biosolids that may be incinerated or disposed on the land, thus contributing to the overall mercury burden in the environment. In addition, any measures that reduce releases to the atmosphere should be encouraged.

Table 6. Suggested content for MMPs based on the type of facility

Type of facility	Suggested content
Publicly (or privately) owned treatment works serving a purely residential area. No dental or medical offices or hospitals. No industrial users.	Recommended distribution of outreach materials on fish-consumption advisories and properly disposing of mercury-containing products.
POTW whose service area contains dental offices.	Recommend or require that dental offices follow American Dental Association BMPs.[a] Collect any bulk mercury in the offices. Develop an approach for using amalgam separators.
POTW whose service area contains one or more hospitals.	Recommend or require that hospitals follow the practices recommended by the American Hospital Association.[b]
POTW whose service area contains schools or medical offices.	Recommend or require that schools and medical offices properly dispose of bulk mercury in their possession (including, for example, mercury-containing sphygmomanometers).
Industrial direct or indirect dischargers that use mercury as an intentional component of their process or recover mercury as a by-product of their process.	Generally, such a case would involve a thorough analysis of opportunities to reduce their releases of mercury.
Industrial direct or indirect dischargers that do not use mercury as an intentional component of their process and do not recover mercury as a by-product of their process.	Such facilities should investigate opportunities to reduce their incidental releases of mercury such as recycling fluorescent lamps, switches, thermostats, etc. and replacing them with low-mercury or non-mercury products.

Notes:

[a] For more information on the American Dental Association BMPs, see Best Management Practices for Amalgam Waste (September 2005) at http://www.ada.org/prof/resources/topics/topics_amalgamwaste.pdf.

[b] For more information on American Hospital Association practices, see Replacing Mercury in Healthcare Facilities—A Step-by-Step Approach at http://www.h2e-online.org/hazmat/mercguide.html.

When developing MMPs, EPA recommends beginning with any existing best management plans and spill prevention and containment control plans for that facility. Many of the activities covered by those plans can also reduce mercury sources to wastewater. After reviewing many pollutant minimization programs, EPA recommends that a plan include at least the following elements:

- Identification and evaluation of current and potential mercury sources
- For POTWs, identification of both large industrial sources and other commercial or residential sources that could contribute large mercury loads to the POTW
- Monitoring to confirm current or potential sources of mercury
- Identification of potential methods for reducing or eliminating mercury, including requiring BMPs or assigning limits to all potential sources of mercury to a collection system, material substitution, material recovery, spill control and collection, waste recycling, process modifications, housekeeping and laboratory use and disposal practices, and public education

- Implementation of appropriate minimization measures identified in the plan
- Effluent monitoring to verify the effectiveness of pollution minimization efforts

EPA believes that these minimum permit conditions may be appropriate because they help to ensure that the discharge does not cause or contribute to an exceedance of water quality standards to protect against possible localized impacts and to minimize the discharge of mercury. EPA also believes that, depending on the particular facts, a permit writer may reasonably conclude that such an MMP is as stringent as necessary to achieve water quality standards.

To further manage mercury discharges, the permitting authority should consider including an effluent trigger level or reduction goal in an MMP. Such a trigger level or goal could be set at a level that would provide a basis for evaluating whether the mercury minimization measures or BMPs specified in the MMP are working as anticipated. The level or goal could be expressed numerically or in narrative form. For example, the MMP might provide a trigger level equal to the existing effluent quality that, if exceeded, would indicate that mercury minimization measures may not be effective. Alternately, the MMP might provide goals for mercury reductions that are expected to occur as a result of the implementation of mercury minimization efforts specified in the MMP. As explained in this section and in section 7.5.2.1, an MMP includes a set of BMPs that would be part of an enforceable special condition of the permit. The MMP might specify that exceeding a trigger level or failing to achieve a mercury reduction goal would prompt actions such as reevaluation of the MMP, additional monitoring, or the implementation of additional BMPs. In this case, the failure of the permittee to undertake the additional actions identified in the MMP would be a violation of the permit special condition.

Even where it is infeasible to calculate a numeric WQBEL (for the reasons discussed in section 7.5.2.1), a permitting authority should consider including in the MMP an enforceable numeric level on the discharge of mercury. In this case, the enforceable numeric level would not constitute a stand-alone water quality-based effluent limit, but rather, a baseline for achieving mercury reductions that, combined with the other measures and practices in the MMP, would together constitute the water quality-based effluent limit. Such an enforceable numeric level could represent either existing effluent quality or a level representing some increment of the mercury reduction determined achievable as a result of the measures and practices specified in the MMP. Depending on the particular facts, the permit writer may reasonably conclude that the enforceable numeric level combined with the other measures and practices in the MMP will result in a level of mercury discharge that is controlled as stringently as necessary to meet water quality standards. Where the MMP contains an enforceable numeric level for mercury and/or methylmercury in the effluent, exceeding that value would be a violation of the permit special condition.

The permitting authorities should consider use of effluent trigger levels, effluent reduction goals, and enforceable numeric levels in any discharge permits that are based on MMPs as water quality-based effluent limits. EPA recommends that permitting authorities include such levels or goals in permits where direct water inputs are relatively high.

8 Related Programs

8.1 What are EPA and others doing as a whole to address mercury?

A wide variety of actions are under way in the United States and internationally to address mercury contamination. EPA's mercury Web site, at http://www.epa.gov/mercury, provides a broad range of information about mercury: actions by EPA and others, including international actions, effects on people and the environment, and how people can protect themselves and their families.

With respect to EPA's actions, on July 5, 2006, EPA issued a report titled *EPA's Roadmap for Mercury* ("*Roadmap*"). It is at http://www.epa.gov/mercury/roadmap.htm. EPA's *Roadmap* describes the Agency's progress to date in addressing mercury issues domestically and internationally, and it outlines EPA's major ongoing and planned actions to address risks associated with mercury. The *Roadmap* describes the Agency's most important actions to reduce both mercury releases and human exposure to mercury. Creating the *Roadmap* has enabled EPA to maximize coordination of its many diverse efforts, with the goal of improving its mercury program. In addition to providing a roadmap for EPA, the report provides important information about mercury to other federal agencies; to EPA's partners in state, tribal, and local governments; and to the public.

8.2 How does pollution prevention play a role in the methylmercury criterion?

Under the national pretreatment program, POTWs routinely control the volume and concentration of pollutants contributed by significant industrial users (SIUs)[24] to their collection system and wastewater treatment plant. However, as water quality criteria, sludge standards, and air emissions standards become more restrictive, even low levels of pollutants like mercury might cause noncompliance with these standards. Therefore, POTWs must expand pollutant control efforts or install treatment technologies to remove the problem pollutants.

In many cases, large-scale treatment technology is either not yet available or not economically feasible for controlling mercury at POTWs. Instead, POTWs are choosing to develop and implement pollution prevention (P2) strategies to reduce the amount of mercury received by the wastewater treatment plant. Although SIUs can contribute a significant mercury load to the treatment plant, non-SIU sources can also be identified as causing or contributing to the problem. For example, the Western Lake Superior Sanitary District (WLSSD) determined that one SIU and many small non-SIUs (dental facilities)

[24] EPA defines an SIU as (1) any industrial user (IU) subject to a categorical pretreatment standard (national effluent guidelines); (2) any user that discharges an average of 25,000 gallons per day or more of process wastewater or that contributes a process waste stream making up 5 percent or more of the average dry weather hydraulic or organic capacity of the POTW treatment plant; or (3) any other user designated by the Control Authority (POTW) to be an SIU on the basis that it has a reasonable potential for adversely affecting the POTW's operation or for violating a pretreatment standard or requirement (40 CFR 403.4(v)).

contribute a major portion of the mercury in its wastewater. Sectors historically more difficult to control (e.g., residential) or beyond the POTW's direct control (e.g., pollutants in contaminated inflow/rainfall) can also contribute substantial loadings.

Effective mercury source reduction relies on the POTW's effectively communicating to sector entities that minimal individual efforts can collectively reduce the mercury loading to the environment. Forming partnerships and working with sector representatives to investigate mercury sources, explore alternatives, and assist in implementing selected options is integral to a successful reduction strategy. Permitting authorities developing a P2 plan should consider a POTW's role in compliance assistance. The sections below provide summary-level guidance for developing a POTW P2 plan.

Through the pretreatment program, POTWs should communicate with their permitting authority, as well as maintain close contact with local sewer dischargers and have a good understanding of specific industrial process operations. Thus, they can uniquely promote P2 to numerous facilities and provide public awareness and education. In general, the success of a POTW P2 effort depends on a behavioral change on the part of the POTW and the community. As noted by the City of Palo Alto, "Experience shows that people are more likely to change their behaviors if they fully understand environmental problems and the range of possible solutions, if they have participated in the process leading to a policy decision, and if they believe regulators are dealing with them in good faith...." (City of Palo Alto 1996). A POTW might minimize community resistance and apathy by undertaking the following activities prior to developing its plan:

- Conduct a preliminary investigation of the problem and potential sources. Verify that the problem is not a wastewater treatment plant operational issue. Identify internal sources and any area government facilities in addition to industrial, commercial, and uncontrollable sources that could be contributing to or causing the problem.

- Meet with upper management (e.g., utility director, mayor, council) and discuss the problem, preliminary findings, and potential ramifications. Upper management support will be essential for obtaining necessary resources, funding, equipment, and authority for implementing a P2 plan. Their support will also be necessary for resolving any wastewater treatment plant and government facility issues. Upper management may also advise development of a POTW mission statement that declares goals and the chosen approach. Exhibit 1 provides an example of the WLSSD mission statement (WLSSD 1997).

- Establish a workgroup composed of representatives from government, industry, community, and environmental organizations, preferably those that are familiar with P2 strategies or with the pollutant of concern. The workgroup likely will develop or help develop the plan, guide plan implementation, and measure plan success. Therefore, findings from the preliminary investigation will guide the POTW to select appropriate committee members and experts. Bear in mind that the workgroup size should ensure representation of most interests but not grow so large as to be counterproductive. This group could also prove valuable in disseminating information.

With the support and expertise needed, the POTW and workgroup can draft a plan by doing the following:

- *State the problem* to provide background information about the POTW, problems caused by mercury, and why the POTW is taking action (described in terms that most people can understand).
- *Identify the goals* to determine whether the POTW intends to help minimize mercury introduced to all environmental media (air, water, solid waste), known as "front-end" P2 or merely to minimize the amount of mercury discharged to the wastewater treatment plant. The latter option ignores mercury transfers to other media (e.g., air, solid waste) and is the less environmentally sound option. It may be essential for the POTW to implement a front-end P2 approach and establish waste collection programs for the proper recycling or disposal of mercury-bearing wastes (e.g., thermometers, fluorescent light bulbs).
- Define an approach that outlines the sectors selected for P2 efforts, the criteria for targeting efforts (e.g., size of the source loading, authority available to control the source or sector, time necessary to produce desired results), where efforts will be voluntary or mandatory, who will execute the various program efforts, and how the POTW will proceed where mercury introduction is beyond its control (e.g., contaminated stormwater).
- Identify resources necessary to implement the plan such as staffing, equipment, and funding.
- Create contingency plans that describe actions to be taken if the planned efforts do not succeed, such as obtaining the authority to mandate and enforce P2 or other source control requirements or installing wastewater treatment plant technology.

Plans might develop in response to a specific problem (e.g., elevated mercury levels in wastewater treatment plant effluent) or proactively to minimize potential problems. Plans will vary in complexity and in resources necessary to achieve goals. Plan updates should detail successful and failed efforts, such as in the form of lessons learned.

Exhibit 1. Example Mission Statement

The WLSSD Commitment to Zero Discharge

The WLSSD as a discharger to Lake Superior is committed to the goal of zero discharge of persistent toxic substances and will establish programs to make continuous progress toward that goal. The District recognizes step-wise progress is only possible when pollution prevention strategies are adopted and rigorously pursued. These approaches will focus upon our discharge as well as indirect sources.

WLSSD will work with its users to implement programs, practices, and policies which will support the goal. We will call upon the resources and assistance of the State and federal governments for support, including financial support of the programs to ensure that our users are not penalized unfairly.

WLSSD recognizes that airborne and other indirect sources beyond District control must be addressed in order for significant reductions to occur.

8.3 What regulations has EPA issued pursuant to the CAA to address air emissions of mercury?

As rules and standards pursuant to the CAA have been developed, proposed, and promulgated since the Amendments of 1990, compliance by emitting sources and actions taken voluntarily have already begun to reduce mercury emissions to the air across the country. EPA expects that a combination of ongoing activities will continue to reduce such emissions over the next decade.

EPA has made substantial progress in addressing mercury air emissions under the CAA. In particular, EPA has issued regulations addressing the major contributors of mercury to the air (including, for example, municipal waste combustors; hospital, medical, and infectious waste incinerators; chlor-alkali plants; and hazardous waste combustors). EPA issued regulations for these source categories under different sections of the CAA, including sections 111, 112, and 129. Indeed, as the result of EPA's regulatory efforts, the United States achieved a 58 percent reduction in domestic mercury air emissions between 1990 and 2005 (see figure 4 and http://cfpub.epa.gov/eroe/index.cfm?fuseaction=detail.viewMidImg&lShowInd=0&subtop=341&lv=list.listByAlpha&r=216615#11215).

The relevant regulations that EPA has issued to date under the CAA are described briefly below. For more information about other CAA actions to control mercury, see http://www.epa.gov/mercury under "What EPA and Others Are Doing."

8.3.1 Municipal waste combustors

In 1995 EPA promulgated new source performance standards (NSPS) that apply to all new municipal waste combustor units (both waste-to-energy plants and incinerators) with the capacity to burn more than 250 tons of municipal solid waste, including garbage, per day and emission guidelines that apply to existing units with the same capacity through either an EPA-approved State plan or a promulgated Federal plan (see 60 FR 65,415 [December 19, 1995], codified at 40 CFR part 60, subparts Eb and Cb). These regulations cover approximately 130 existing waste-to-energy plants and incinerators, as well as any new plants and incinerators built in the future. The regulations have reduced emissions of a number of HAPs, including mercury, by approximately 145,000 tons per year. The regulations have resulted in about a 90 percent reduction in mercury emissions from domestic municipal waste combustors from 1990 emission levels (57 tons per year of mercury emitted from domestic municipal waste combustors in 1990 versus 2.3 tons per year in 2005). In 2000, EPA promulgated NSPS and emission guidelines establishing similar requirements for small municipal waste combustor units (units with a capacity of 35 to 250 tons per day) (see 65 FR 76,355 [December 6, 2000], codified at 40 CFR part 60, subparts AAAA and BBBB).

8.3.2 Hospital, medical, and infectious waste incinerators

Hospital/medical/infectious waste incinerators (HMIWIs) are used by hospitals, health care facilities, research laboratories, universities, and commercial waste disposal companies to dispose of hospital waste and/or medical/infectious waste. EPA adopted regulations controlling mercury and other emissions from HMIWIs on September 15, 1997 (62 FR 48,348, codified at 40 CFR part 60, subparts Ce and Ec). All existing HMIWIs were required to comply with the regulations by September 15, 2002. EPA estimated that the regulations would reduce mercury emissions from HMIWIs at existing facilities by 93–95 percent (from 16.5 to 0.9-1.2 tons per year). In fact, the actual mercury emission reductions achieved as a result of implementing the regulations were approximately 98 percent. At the time the regulations were issued, EPA expected that 50 to 80 percent of the 2,400 then-existing HMIWIs would close in response to the rule. EPA's rule resulted in a significant change in medical waste disposal practices in the United States. Because of the increased cost of on-site incineration under the 1997 rule, approximately 98 percent of the 2,400 HMIWIs operating at health care facilities in 1997

have shut down or obtained exemptions, and few facilities have installed new HMIWIs (5 new HMIWIs at 4 facilities). Instead, many facilities have switched to other methods of waste treatment and disposal, such as autoclaving and off-site commercial waste disposal. There are currently 57 existing HMIWIs operating at 52 facilities. EPA adopted revised regulations for HMIWIs on October 6, 2009 (74 FR 51,368). The revisions were issued in order to respond to a court remand of the 1997 rule and to satisfy the Clean Air Act section 129(a)(5) requirement to conduct a review of the standards every 5 years. EPA estimates that the revised regulations will reduce mercury emissions at existing HMIWIs by 89 percent (from 0.3 to 0.04 tons per year). The revised mercury standards are estimated to impact 20 HMIWIs, which are expected to employ mercury control technology (e.g., installing activated carbon injection systems or increasing current use of activated carbon). All existing HMIWIs are required to comply with the revised regulations by October 6, 2014.

8.3.3 Chlor-alkali plants

On December 19, 2003, EPA issued final regulations to reduce mercury emissions from chlorine production plants that rely on mercury cells (see 68 FR 70,904, codified at 40 CFR part 63, subpart IIIII). These air regulations have reduced mercury air emissions from existing chlor-alkali plants by approximately 50 percent since the compliance date of December 19, 2006. The regulation requires a combination of controls for point sources, such as vents, and BMPs to address fugitive air emissions, that are more stringent work practices than those required by a preexisting regulation that covered this source category. Today, there are four (4) such plants in the United States, compared to 20 when work on the rule began. In addition, EPA completed a study of fugitive mercury emissions at existing chlor-alkali plants and found the levels of elemental mercury emissions much lower than previously thought. Current total emissions from the four plants are estimated to be approximately 0.3 tons per year of mostly (>98%) elemental mercury.

8.3.4 Hazardous waste combustors

In 2005, EPA published standards under Section 112(d) of the CAA for hazardous waste combustors (HWCs)--incinerators, cement kilns, lightweight aggregate kilns, liquid fuel boilers, solid fuel boilers, and hydrochloric acid production furnaces that burn hazardous waste (70 FR 59402 (October 12, 2005)). The mercury standards for existing and new sources, respectively, are under 40 CFR 63.1216(a)(2) and (b)(2) for solid fuel boilers, 40 CFR 63.1217(a)(2) and (b)(2) for liquid fuel boilers, 40 CFR 63.1218(a)(2) and (b)(2) for hydrochloric acid production furnaces, 40 CFR 63.1219(a)(2) and (b)(2) for incinerators, 40 CFR 63.1220(a)(2) and (b)(2) for cement kilns, and 40 CFR 63.1221(a)(2) and (b)(2) for lightweight aggregate kilns. Approximately 200 HWCs are complying with these standards.

EPA will be reviewing these standards as a result of the D.C Circuit Court of Appeals' approval in June 2009 of EPA’s motion for voluntary remand of the emission standards. Any revised standards would be no less stringent than the current standards.

8.3.5 Coal-fired power plants

At present, the largest single source of anthropogenic mercury emissions in the country is coal-fired power plants. Mercury emissions from U.S. power plants are estimated to account for about one percent of total global mercury emissions (70 FR 15994; March 29, 2005). EPA has initiated a rulemaking effort to develop emission standards under Clean Air Act section 112(d) for emissions of hazardous air pollutants (including mercury) from coal- and oil-fired electric utility steam generating units. Consistent with a Consent Decree, the Agency intends to issue final emission standards for these units by the end of 2011.

8.3.6 Other

In addition to EPA's regulatory efforts under the CAA, in 1996 the United States eliminated the use of mercury in most batteries under the Mercury Containing and Rechargeable Battery Management Act. This action reduces the mercury content of the waste stream, which further reduces mercury emissions from waste combustion. In addition, voluntary measures to reduce use of mercury-containing products, such as the voluntary measures to which the American Hospital Association has committed, will contribute to reduced emissions from waste combustion.

9 References

Akagi, H., O. Malm, Y. Kinjo, M. Harada, F.J.P. Branches, W.C. Pfeiffer, and H. Kato. 1995. Methylmercury pollution in the Amazon, Brazil. *Sci. Total Environ*. 175:85–95.

Ambrose, R.B., Jr., T.A. Wool, J.P. Connolly, and R.W. Schanz. 1988. *WASP4, A Hydrodynamic and Water Quality Model—Model Theory, User's Manual and Programmer's Guide*. EPA-600-3-87-039. Athens, Georgia: U.S. Environmental Protection Agency, Environmental Research Laboratory.

Amorim, M.I.M., D. Mergler, M.O. Bahia, H. Dubeau, D. Miranda, J. Lebel, R.R. Burbano, and M. Lucotte. 2000. Cytogenetic damage related to low levels of methyl mercury contamination in the Brazilian Amazon. *An. Acad. Bras. Ciênc*. 72(4): 497–507.

AMSA (Association of Metropolitan Sewerage Agencies). 2000. *Evaluation of Domestic Sources of Mercury*. Association of Metropolitan Sewerage Agencies, Washington, DC.

Atkeson, T., D. Axelrad, C. Pollman, and G. Keeler. 2002. *Integrating Mercury Deposition and Aquatic Cycling in the Florida Everglades*. Tallahassee: Florida Department of Environmental Protection. <ftp://ftp.dep.state.fl.us/pub/labs/assessment/mercury/tmdlreport03.pdf>

ATSDR (Agency for Toxic Substances and Disease Registry). 1999. Toxicological Profile for Mercury. Atlanta, Georgia: U.S. Department of Health and Human Services, Public Health Service.

AZDEQ (Arizona Department of Environmental Quality). 1999. *Total Maximum Daily Load and Implementation Plan for Mercury, Arivaca Lake, Arizona*. Phoenix, Arizona: Arizona Department of Environmental Quality, EPA Region 9, and Tetra Tech, Inc.

Baeyens, W., C. Meuleman, B. Muhaya, M. Leermakers. 1998. Behaviour and speciation of mercury in the Scheldt Estuary (water, sediments and benthic organisms). *Hydrobiologia* 366:63–79.

Balogh, S.J., M.L. Meyer, and D.K. Johnson. 1998. Transport of mercury in three contrasting river basins. *Environ. Sci. Technol*. 32:456–462.

Barber, M.C. 2002. *Bioaccumulation and Aquatic System Simulator (BASS) User's Manual, Beta Test Version 2.1*. EPA-600-R-01-035. Athens, Georgia: U.S. Environmental Protection Agency, Office of Research and Development, Ecosystems Research Division.

Barkay, T., S.M. Miller, and A.O. Summers. 2003. Bacterial mercury resistance from atoms to ecosystems. *FEMS Microbiol. Rev.* 27:355–384.

Becker, D.S. and G.N. Bigham. 1995. Distribution of mercury in the aquatic food web of Onondaga Lake, New York. *Water Air Soil Poll.* 80:563–571.

Benoit, J.M., C.C. Gilmour, R.P. Mason, G.S. Riedel, and G.F. Riedel. 1998. Behavior of mercury in the Patuxent River estuary. *Biogeochemistry* 40:249–265.

Benoit, J.M., C.C. Gilmour, A. Heyes, R.P. Mason, and C. Miller. 2003. Geochemical and biological controls over methylmercury production and degradation in aquatic systems, in *Biogeochemistry of Environmentally Important Trace Metals*. ACS Symposium Series 835.

Bigham, G.N. and G.M. Vandal. 1994. A drainage basin perspective of mercury transport and bioaccumulation: Onondaga Lake, New York. Twelfth International Neurotoxicology Conference, Hot Springs, Arkansas.

Bloom, N.S. 1989. Determination of picogram levels of methylmercury by aqueous phase ethylation, followed by cryogenic gas chromatography with cold vapor atomic fluorescence detection. *Can. J. Fish. Aquat. Sci.* 46:1131–1140.

Bloom, N.S. 1992. On the chemical form of mercury in edible fish and marine invertebrate tissue. *Can. J. Fish. Aquat. Sci.* 49:1010–1017.

Bloom, N.S. and E.A. Crecelius. 1983. Determination of mercury in seawater at sub-nanogram per liter levels. *Mar. Chem.* 14:49–59.

Bloom, N.S. and W.F. Fitzgerald. 1988. Determination of volatile mercury species at the picogram level by low temperature gas chromatography with cold vapor atomic fluorescence detection. *Anal. Chim. Acta*. 208:151–161.

Brumbaugh, W.G., D.P. Krabbenhoft, D.R. Helsel, J.G. Wiener, and K.R. Echols. 2001. *A National Pilot Study of Mercury Contamination of Aquatic Ecosystems Along Multiple Gradients: Bioaccumulation in Fish*. Biological Science Report: USGS/BRD/BSR-2001-0009. Columbia, Missouri: U.S. Geological Survey, Columbia Environmental Research Center.

Bullock, O. and K. Brehme. 2002. Atmospheric Mercury Simulation Using the CMAQ Model: Formulation Description and Analysis of Wet Deposition Results. *Atmosph. Environ.* 36:2135–2146.

Burkhard, L.P. 2003. Factors influencing the design of BAF and BSAF field studies. *Environ. Toxicol. Chem*. 22:351–360.

Burkhard, L.P., D.E. Endicott, P.M. Cook, K.G. Sappington, and E.L. Winchester. 2003. Evaluation of two methods for prediction of bioaccumulation factors. *Environ. Sci. Technol.* 37(20):4626–4634.

Burrows, W.C. and P.A. Krenkel. 1973. Studies on uptake and loss of methylmercury-203 by bluegills (*Lepomis marcochirus* Raf.). *Environ. Sci. Technol.* 7(13):1127–1130.

Byun, D.W. and J.K.S. Ching, eds, 1999. *Science Algorithms of EPA Models-3 Community Multiscale Air Quality (CMAQ) Modeling System*. EPA/600/R-99/030. Washington, DC: U.S. Environmental Protection Agency, Office of Research and Development.

Byun, D.W. and K.L. Schere. 2006. Review of the governing equations, computational algorithms, and other components of the Models-3 Community Multiscale Air Quality (CMAQ) modeling system. *J. Applied Mech. Rev.* 59(2):51–77.

Cambell, K.R., C.J. Ford, and D.A. Levine. 1998. Mercury fistribution in Poplar Creek, Oak Ridge, Tennessee, USA. *Environ. Chem.* 17:1191–1198.

Carpi, A. and S.E. Lindberg. 1997. Sunlight-mediated emission of elemental mercury from soil amended with municipal sewage sludge. *Environ. Sci. Technol.* 31(7):2085–2091.

CDC (Centers for Disease Control and Prevention). 2005. *Third National Report on Human Exposure to Environmental Chemicals*. NCEH pub no. 05-0725. Atlanta, Georgia: Centers for Disease Control and Prevention. <http://www.cdc.gov/exposurereport>

Central Valley Water Board. 2005. Amendments to the Water Quality Control Plan for the Sacramento River and San Joaquin River Basins for the Control of Mercury in Cache Creek, Bear Creek, Sulphur Creek, and Harley Gulch. Final Report. Rancho Cordova, California: California Regional Water Quality Control Board, Central Valley Region. <http://www.swrcb.ca.gov/rwqcb5/board_decisions/adopted_orders/resolutions/r5-2005-0146.pdf>.

City of Palo Alto. 1996. Public Participation/Community Education. Palo Alto, California: Palo Alto Regional Water Quality Control Plant.

Cizdziel, J.V., T.A. Hinners, J.E. Pollard, E.M. Heithmar, and C.L. Cross. 2002. Mercury concentrations in fish from Lake Mead, USA, related to fish size, condition, trophic level, location, and consumption risk. *Arch. Environ. Contam. Toxicol*. 43:309–317.

Cizdziel, J.V., T.A. Hinners, C.L. Cross, and J.E. Pollard. 2003. Distribution of mercury in the tissues of five species of freshwater fish from Lake Mead, USA. 2003. *J. Environ. Monit.* 5:802–807.

Cleckner, L.B., E.S. Esseks, P.G. Meier, and G.J. Keeler. 1995. Mercury concentrations in two great waters. *Water Air Soil Poll.* 80:581–584.

Dennis, R.L., D.W. Byun, J.H. Novak, K.J. Galluppi, C.J. Coats, and M.A. Vouk. 1996. The next generation of integrated air quality modeling: EPA's Models-3, *Atmos. Environ.* 30:1925–1938.

DeWild, J.F., M.L. Olson, and S.D. Olund. 2002. Determination of methyl mercury by aqueous phase ethylation, followed by gas chromatographic separation with cold vapor atomic fluorescence detection. U.S. Geological Survey Open-File Report 01-445. Middleton, Wisconsin: U.S. Geological Survey.

Doyon, J.F., R. Schentagne, and R. Verdon. 1998. Different mercury bioaccumulation rates between sympatric populations of dwarf and normal lake whitefish (*Coregonus clupeaformis*) in the La Grande complex watershed, James Bay, Quebec. *Biogeochemistry* 40:203–216.

EPRI (Edison Power Research Institute). 1999. *Dynamic Mercury Cycling Model for Win95/NT: A Model for Mercury Cycling in Lakes*. D-MCM version 1.0. User's guide and technical reference. Lafayette, California: Edison Power Research Institute.

EPRI (Edison Power Research Institute). 2002. *Dynamic Mercury Cycling Model (D-MCM) for Windows 98/NT 4.0/2000/XP: A model for Mercury Cycling in Lakes.* D-MCM Version 2.0. Lafayette, California: Edison Power Research Institute.

Frescholtz, T. and M.S. Gustin. 2004. Soil and foliar mercury emission as a function of soil concentration. *Water Air Soil Poll.* 155:223–237.

FTN (FTN Associates, Ltd.) 2002. *TMDLs for Segments Listed for Mercury in Fish Tissue for the Ouachita River Basin, and Bayou Bartholomew, Arkansas and Louisiana to Columbia.* Little Rock, Arkansas: FTN Associates, Ltd. <http://www.epa.gov/region6/water/ecopro/latmdl/ouarmercury(f).pdf>

Gbundgo-Tugbawa, S. and C.T. Driscoll. 1998. Application of the regional mercury cycling model (RMCM) to predict the fate and remediation of mercury in Onondaga Lake, New York. *Water Air Soil Poll.* 105:417–426.

Giblin, F.J. and E.J. Massaro. 1973. Pharmacodynamics of methylmercury in the rainbow trout (*Salmo gairdneri*): Tissue uptake, distribution and excretion. *Toxicol. Appl. Pharm.* 24(1):81–91.

Gilbert, R.O. 1987. *Statistical Methods for Environmental Pollution Monitoring.* New York: VanNostrand Reinhold Company.

Gilmour, C.C. and E.A. Henry. 1991. Mercury Methylation in Aquatic Systems Affected by Acid Deposition. *Environ. Pollut.* 71:131-149.

Gilmour, C.C., G.S. Reidel, M.C. Ederington, J.T. Bell, J.M. Benoit, G.A. Gill, and M.C. Stordall. 1998. Methylmercury concentrations and production rates across a trophic gradient in the northern Everglades. *Biogeochemistry* 40:327-345.

Glass, G.E., J.A. Sorensen, and G.R. Rapp, Jr. 2001. Methylmercury bioaccumulation dependence on n. pike age and size in twenty Minnesota lakes. *ACS Sym Ser*. 772, *Persistent, Bioaccumulative, and Toxic Chemicals I*, Ch. 11, pp. 150–163.

Greenfield, B.K., T.R. Hrabik, C.J. Harvey, and S.R. Carpenter. 2001. Predicting mercury levels in yellow perch: Use of water chemistry, trophic ecology, and spatial traits. *Can. J. Fish. Aquat. Sci.* 58:1419–1429.

Greenfield J., T. Dai, and H. Manguerra. 2002. Watershed modeling extensions of the watershed characterization system. In *Proceedings of the Water Environment Federation Specialty Conference, Watershed 2002,* Ft. Lauderdale, Florida, February, 2002.

Grell, G., J. Dudhia, and D. Stauffer. 1994. *A Description of the Fifth-Generation Penn State/NCAIR Mesoscale Model (MM5)*. NCAIR/TN-398+STR. Boulder, Colorado: National Center for Atmospheric Research.

Grieb, T. M., C.T. Driscoll, S.P. Gloss, C.L. Schofield, G.L. Bowie, and D.B. Porcella. 1990. Factors affecting mercury accumulation in fish in the Upper Michigan Peninsula. *Environ. Toxicol. Chem.* 9:919–930.

Gustin, M.S., J.A. Ericksen, D.E. Schorran, D.W. Johnson, S.E. Lindberg, and J.S. Coleman. 2004. Application of controlled mesocosms for understanding mercury air-soil-plant exchange. *Environ. Sci. Technol.* 38: 6044–6050.

Hammerschmidt, C.R., J.G. Wiener, B.E. Frazier, and R.G. Rada. 1999. Methylmercury content of eggs in yellow perch related to maternal exposure in four Wisconsin lakes. *Environ. Sci. Technol.* 33:999–1003.

Harris, R., J. Rudd, M. Amyot, C. Babiarz, K. Beaty, P. Blanchfield, R. Bodaly, B. Branfireun, C. Gilmour, J. Graydon, A. Heyes, H. Hintelmann, J. Hurley, C. Kelly, D. Krabbenhoft, S. Lindberg, R. Mason, M. Paterson, C. Podemski, K. Sandilands, G. Southworth, V. St. Louis, and M. Tate. 2006. How does atmospheric mercury deposition affect methylmercury concentrations in a boreal ecosystem: results from the 1st four years of METAALICUS. Abstract from 8th International Conference on Mercury as a Global Pollutant, Madison, Wisconsin, August 8-11, 2006.

Hinners, T.A. 2004. Possible ramifications of higher mercury concentrations in fillet tissue of skinnier fish. 2004 National Forum on Contaminants in Fish, San Diego, California, January 25–28.

Horvat, M., L. Liang, and N.S. Bloom. 1993. Comparison of distillation with other current isolation methods for the determination of methylmercury compounds in low level environmental samples. *Anal. Chim. Acta* 282:153–168.

Hrabik, T.R. and C.J. Watras. 2002. Recent declines in mercury concentration in a freshwater fishery: Isolating the effects of de-acidification and decreased atmospheric mercury deposition in Little Rock Lake. *Sci. Total Environ.* 297:229–237.

Huckabee, J.W., J.W. Elwood, and S.G. Hildebrand. 1979. Accumulation of mercury in freshwater biota. In *The Biogeochemistry of Mercury in the Environment*., ed. J.O. Nriagu. Amsterdam: Elsevier/North-Holland Biomedical Press.

Hurley, J.P., M.M. Shafer, S.E. Cowell, J.T. Overdier, P.E. Hughes, and D.E. Armstrong. 1996. Trace metal assessment of Lake Michigan tributaries using low level techniques. *Environ. Sci. Technol.* 30:2093–2098.

Hurley, J.P., S.E. Cowell, M.M. Shafer, P.E. Hughes. 1998. Partitioning and transport of total and methyl mercury in the Lower Fox River, Wisconsin. *Environ. Sci. Technol.* 32:1424–1432.

ICF International. 2006. Model-Based Analysis and Tracking of Airborne Mercury Emissions to Assist in Watershed Planning. Prepared for U.S. Environmental Protection Agency, Office of Water. San Rafael, California: ICF International.

Jackson, T.A. 1991. Biological and environmental control of mercury accumulation by fish in lakes and reservoirs of northern Manitoba, Canada. *Can. J. Fish. Aquat. Sci.* 48:2449–2470.

Jackson, T.A. 1998. Mercury in aquatic ecosystems. In *Metal Metabolism in Aquatic Environments*, ed. W.J. Langston and M.J. Bebianno, pp. 77–158. London: Chapman & Hall.

Kamman, N., C.T. Driscoll, B. Estabrook, D.C. Evers, and E.K. Miller. 2004. Biogeochemistry of Mercury in Vermont and New Hampshire Lakes: An Assessment of Mercury in Water, Sediment and Biota of Vermont and New Hampshire Lakes. Comprehensive final project report. Waterbury: Vermont Department of Environmental Conservation.

Kannan K., R.G. Smith, R.F. Lee, H.L. Windom, P.T. Heitmuller, J.M. Macauley, and J.K. Summers. 1998. Distribution of total mercury and methylmercury in water, sediment, and fish South Florida estuaries. *Environ. Contam. Toxicol.* 34: 109-118.

Kehrig, H.A., O. Malm, and I. Moreira. 1998. Mercury in a widely consumed fish *Micropogonias furnieri* (Demarest, 1823) from four main Brazilian estuaries. *Sci. Total Environ.* 213:263–271.

Kidd, K., R. Hesslein, R. Fudge, and K. Hallard. 1995. The influence of trophic level as measured by delta-N-15 on mercury concentrations in fresh-water organisms. *Water Air Soil Poll.* 80(1–4):1011–1015.

Kim, J.P. 1995. Methylmercury in rainbow trout (*Oncorhynchus mykiss*) from Lakes Okareka, Okaro, Rotmahana, Rotorua and Tarawera, North Island, New Zealand. *Sci. Total Environ*. 164:209–219.

Landis, M.S., M. Lynam, and R.K. Stevens. 2004. The monitoring and modeling of mercury species in support of local regional and global modeling. In *Dynamics of Mercury Pollution on Regional and Global Scales*, ed. N. Pirrone and K.R. Mahaffey. New York: Kluwer Academic Publishers.

Lasorsa, B.and S. Allen-Gil. 1995. The methylmercury to total mercury ratio in selected marine, freshwater, and terrestrial organisms. *Water Air Soil Poll.* 80:905–913.

Lin, C.J., and S.O. Pehkonen. 1999. The chemistry of atmospheric mercury: A review. *Atmos. Environ.* 33:2067–2079.

Lindberg, S.E., and J.E. Stratton. 1998. Atmospheric mercury speciation: concentrations and behavior of reactive gaseous mercury in ambient air. *Environ. Sci. Technol.* 32(1):49–57.

Mason, R.P. and W.F. Fitzgerald. 1990. Alkylmercury species in the equatorial Pacific. *Nature* 347:457–459.

Mason, R.P. and A.L. Lawrence. 1999. Concentration, distribution, and bioavailability of mercury and methylmercury in sediments of Baltimore Harbor and Chesapeake Bay, Maryland, USA. *Environ. Toxicol. Chem.* 18(11):2438–2447.

Mason, R.P., F.M.M. Morel, and H.F. Hemond. 1995. The role of microorganisms in elemental mercury formation in natural waters. *Water Air Soil Poll.* 80:775–787.

Mason, R.P. and K.A. Sullivan. 1997. Mercury in Lake Michigan. *Environ. Sci. Technol.* 31:942–947.

Mason, R.P. and K.A. Sullivan. 1998. Mercury and methylmercury transport though an urban watershed. *Water Res.* 32:321–330.

McKim, J.M., G.F. Olson, G.W. Holcombe, and EP. Hunt. 1976. Long-tem effects of methylmercuric chloride on three generations of brook trout (*Salvelinus fontinalis*): toxicity, accumulation, distribution, and elimination. *J. Fish. Res. Board Can.* 33:2726–2739.

McNally, D. 2003. Annual Application of MM5 for Calendar Year 2001. Topical report submitted to U.S. Environmental Protection Agency. March.

Mierle, G. and R. Ingram. 1991. The role of humic substance in the mobilization of mercury from watersheds. *Water Air Soil Poll.* 56:349–357.

MPCA (Minnesota Pollution Control Agency). 2007. *Minnesota Statewide Mercury Total Maximum Daily Load*. Minnesota Pollution Control Agency, Minneapolis, Minnesota. < http://proteus.pca.state.mn.us/publications/wq-iw4-01b.pdf>

Monson, B.A. and P.L. Brezonik. 1998. Seasonal patterns of mercury species in water and plankton from softwater lakes in northeastern Minnesota. *Biogeochemistry* 40:147–162.

Morel, F., A.M.L. Kraepiel, and M. Amyot. 1998. The chemical cycle and bioaccumulation of mercury. *Annu. Rev. Ecol. Syst.* 29:543–566.

Neter, J., M.H. Kutner, C.J. Nachtsheim, and W. Wasserman. 1996. *Applied Linear Statistical Models*, 4th ed. Chicago: Irwin.

Niessen, S., N. Mikac, and J.C. Fischer. 1999. Microwave-assisted determination of total mercury and methylmercury in sediment and porewater. *Analysis* 27:871–875.

NRC (National Research Council). 2000. *Toxicological Effects of Methylmercury*. National Research Council, Committee on the Toxicological Effects of Methylmercury. Washington, DC: National Academy Press.

Park, J.G. and L.R. Curtis. 1997. Mercury distribution in sediments and bioaccumulation by fish in two Oregon reservoirs: Point-source and nonpoint-source impacted systems. *Arch. Environ. Contam. Toxicol.* 33:423-429.

Parsons Corporation. 2005. *TMDLs for Mercury in Fish Tissue for Coastal Bays and Gulf Waters of Louisiana*. Prepared for U.S. Environmental Protection Agency, Region 6, Dallas, Texas, and the Office of Environmental Assessment, Louisiana Department of Environmental Quality. Austin, Texas: Parsons Corporation.

Peterson, S.A., J. van Sickle, A.T. Herlihy, and R.M. Hughes. 2007. Mercury concentration in fish from streams and rivers throughout the western United States. *Environ. Sci. Technol*. 41:58–65.

Phillips, P.T. 1980. *Quantitative Aquatic Biological Indicators. Pollution Monitoring Series*. London: Applied Science Publishers Ltd.

QEA (Quantitative Environmental Analysts, LLC). 2000. *Bioaccumulation model QUAFDCHN*. Version 1.0. Montvale, New Jersey: Quantitative Environmental Analysts, LLC.

Rae, D. 1997. *Impacts of mercury reductions in Minnesota*. Prepared for Minnesota Pollution Control Agency. September 30.

Rasmussen, P.E. 1994. Current methods of estimating atmospheric mercury fluxes in remote areas. *Environ. Sci. Technol.* 28(13):2233–2241.

Rodgers, D.W. and F.W.H. Beamish. 1982. Dynamics of dietary methylmercury in rainbow trout, *Salmo Gairdneri*. *Aquat. Toxicol.* 2:271–290.

Salonen, J.T., K. Seppanen, K. Nyyssonen, H. Korpela, J. Kauhanen, M. Kantola, J. Tuomilehto, H. Esterbauer, F. Tatzber, and R. Salonen. 1995. Intake of mercury from fish, lipid peroxidation, and the risk of myocardial infarction and coronary, cardiovascular, and any death in Eastern Finnish men. *Circulation* 91(3):645–655.

Sanborn, J.R. and R.K. Brodberg. 2006. *Evaluation of Bioaccumulation Factors and Translators for Methylmercury*. California Environmental Protection Agency, Office of Environmental Health Hazard Assessment. March 2006.

Scholtz, M.T., B.J.V. Heyst, and W.H. Schroeder. 2003. Modeling of mercury emissions from background soils. *Sci. Total Environ.* 304:185–207.

Schroeder, W.H., J. Munthe, J. and O. Lindqvist. 1989. Cycling of mercury between water air and soil compartments of the environment. *Water Air Soil Poll.* 48:337–347.

Sellers, P., C.A. Kelly, J.W.M. Rudd, and A.R. MacHutchon. 1996. Photodegradation of methylmercury in lakes. *Nature* 380:694.

Silva I.A., J.F. Nyland, A. Gorman, A. Perisse, A.M. Ventura, E.C. Santos, J.M. de Souza, C.L. Burek , N.R. Rose, and E.K. Silbergeld. 2004. Mercury exposure, malaria, and serum antinuclear/antinucleolar antibodies in Amazon populations in Brazil: A cross-sectional study. *Environ. Health* 3(1):11.

Slotton, D. G., J. E. Reuter, and C.R. Goldman. 1995. Mercury uptake patterns of biota in a seasonally anoxic northern California reservoir. *Water Air Soil Poll.* 80(1–4): 841–850.

Slotton, D.G., S.M. Ayers, T.H. Suchanek, R.D. Weyland, A.M. Liston. 2004. *Mercury Bioaccumulation and Trophic Transfer in the Cache Creek Watershed, California, in Relation to Diverse Aqueous Mercury Exposure Conditions. Subtask 5B. Final report*. Prepared for the CALFED Bay-Delta Program, Directed Action #99-B06. Davis: University of California–Davis, Dept. of Env. Science and Policy and Dept. Wildlife, Fish and Conservation Biology.

Soneston, L. 2003. Fish mercury levels in lakes—Adjusting for Hg and fish-size covariation. *Environ. Pollut.* 125:255–265.

Sorensen, J.A., G.E. Glass, K.W. Schmidt, J.K. Huber, and G.R. Rapp, Jr. 1990. Airborne mercury deposition and watershed characteristics in relation to mercury concentrations in water, sediments, plankton, and fish of eighty northern Minnesota lakes. *Environ. Sci. Technol.* 24(11):1716–1727.

St. Louis, V., J.W.M. Rudd, C.A. Kelly, B.D. Hall, K.R. Rolfhus, K.J. Scott, S.E. Lindberg, and W. Dong. 2001. Importance of the forest canopy to fluxes of methyl mercury and total mercury to boreal ecosystems. *Environ. Sci. Technol.* 35:3089–3098.

Szefer, P., M. Domaga-a-Wieloszewska, J. Warzocha, A. Garbacik-Weso-owska, and T. Ciesielski. 2003. Distribution and relationships of mercury, lead, cadmium, copper and zinc in perch (*Perca fluviatilis*) from the Pomeranian Bay and Szczecin Lagoon, southern Baltic. *Food Chem.* 81(1):73–83.

Tetra Tech, Inc. 2001. *Total Maximum Daily Load for Mercury in McPhee and Narraguinnep Reservoirs, Colorado*. Prepared for U.S. Environmental Protection Agency, Region 8. Fairfax, Virginia: Tetra Tech, Inc.

Ullrich, S.M., T.W. Tanton, and S.A. Abdrashitova. 2001. Mercury in the aquatic environment: A review of factors affecting methylation. *Crit. Rev. Env. Sci. Tec.* 31:241–293.

USDA/ARS (U.S. Department of Agriculture, Agricultural Research Service). 1998. *1994–1996 Continuing Survey of Food Intakes by Individuals and 1994–1996 Diet and Health Knowledge Survey*. CD–ROM, accession number PB98–500457. [Available from the National Technical Information Service, 5285 Port Royal Road, Springfield, VA 22161; phone: 703-487-4650.]

USDA/ARS (U.S. Department of Agriculture, Agricultural Research Service). 2000. 1994–1996, 1998 Continuing Survey of Food Intakes by Individuals. CD–ROM, accession number PB98–500457. [Available from the National Technical Information Service, 5285 Port Royal Road, Springfield, VA 22161; phone: 703-487-4650.]

USEPA (U.S. Environmental Protection Agency). 1983. *Technical Support Manual: Waterbody Surveys and Assessments for Conducting Use Attainability Analyses*. Washington, DC: U.S. Environmental Protection Agency, Office of Water. <http://www.epa.gov/waterscience/library/wqstandards/uaavol123.pdf>

USEPA (U.S. Environmental Protection Agency). 1991. *Technical Support Document for Water Quality-based Toxics Control*. EPA 505/2-90-001. Washington, DC: U.S. Environmental Protection Agency, Office of Water Enforcement and Permits and Office of Water Regulations and Standards. <http://www.epa.gov/npdes/pubs/owm0264.pdf>

USEPA (U.S. Environmental Protection Agency). 1994. *Water Quality Standards Handbook*. EPA-823-B-94-005a&b. Washington, DC: U.S. Environmental Protection Agency, Office of Water. <http://www.epa.gov/waterscience/standards/handbook>

USEPA (U.S. Environmental Protection Agency). 1995a. *Final Water Quality Guidance for the Great Lakes System*. 60 FR 15366. Washington, DC: U.S. Environmental Protection Agency.

USEPA (U.S. Environmental Protection Agency). 1995b. *Interim Economic Guidance for Water Quality Standards: Workbook*. EPA 823/B-95-002. Washington, DC: U.S. Environmental Protection Agency, Office of Water. <http://www.epa.gov/waterscience/standards/econworkbook>

USEPA (U.S. Environmental Protection Agency). 1995c. *Great Lakes Water Quality Initiative Technical Support Document for the Procedure to Determine Bioaccumulation Factors*. EPA 820/B-95-005. Washington, DC: U.S. Environmental Protection Agency, Office of Water.

USEPA (U.S. Environmental Protection Agency). 1996a. *Method 1669: Sampling Ambient Water for Trace Metals at EPA Water Quality Criteria Levels*. EPA-821-R-96-011. Washington, DC: U.S. Environmental Protection Agency, Office of Science and Technology.

USEPA (U.S. Environmental Protection Agency). 1996b. *NPDES Permit Writers' Manual*. EPA-833-B-96-003. Washington, DC: U.S. Environmental Protection Agency, Office of Wastewater Management. <http://www.epa.gov/npdes/pubs/owm0243.pdf>

USEPA (U.S. Environmental Protection Agency). 1997a. *Mercury Study Report to Congress.* Volume VII: *Characterization of Human Health and Wildlife Risks from Mercury Exposure in the United States*. EPA-452/R-97-009. Washington, DC: U.S. Environmental Protection Agency. <http://www.epa.gov/ttn/oarpg/t3/reports/volume7.pdf>

USEPA (U.S. Environmental Protection Agency). 1997b. *Mercury Study Report to Congress.* Volume I: Executive Summary. EPA-452/R-97-003. Washington, DC: U.S. Environmental Protection Agency. <http://www.epa.gov/ttn/oarpg/t3/reports/volume1.pdf>

USEPA (U.S. Environmental Protection Agency). 1997c. *Mercury Study Report to Congress.* Volume III: *Fate and Transport of Mercury in the Environment*. EPA-452/R-97-005. Washington, DC: U.S. Environmental Protection Agency. <http://www.epa.gov/ttn/oarpg/t3/reports/volume3.pdf>

USEPA (U.S. Environmental Protection Agency). 1997d. *Exposure Factors Handbook*. EPA/600/P-95/002Fa-c. Washington, DC: U.S. Environmental Protection Agency, Office of Research and Development.

USEPA (U.S. Environmental Protection Agency). 1997e. *Establishing Site Specific Aquatic Life Criteria Equal to Natural Background.* Washington, DC: U.S. Environmental Protection Agency, Office of Water.

USEPA (U.S. Environmental Protection Agency). 1997f. *Mercury Study Report to Congress.* Volume IV: *An Assessment of Exposure to Mercury in the United States.* EPA-452/R-97-005. Washington, DC: U.S. Environmental Protection Agency. < http://www.epa.gov/ttn/oarpg/t3/reports/volume4.pdf>

USEPA (U.S. Environmental Protection Agency). 1998a. *Guidance for Conducting Fish and Wildlife Consumption Surveys*. EPA 823-B-98-007. Washington, DC: U.S. Environmental Protection Agency, Office of Water. <http://www.epa.gov/waterscience/fish/fishguid.pdf>

USEPA (U.S. Environmental Protection Agency). 1998b. *Results of the EPA Method 1631 Validation Study, February, 1998*. Washington, DC: U.S. Environmental Protection Agency.

USEPA (U.S. Environmental Protection Agency). 1999a. *Hazardous Air Pollutants Inventory—Final*, 1999 National Emission Inventory, Version 3.0. Washington, DC: U.S. Environmental Protection Agency. < http://www.epa.gov/ttn/chief/net/1999inventory.html#final3haps>.

USEPA (U.S. Environmental Protection Agency). 1999b. *Overview of P2 Approaches at POTWs*. Draft. Washington, DC: U.S. Environmental Protection Agency, Office of Water.

USEPA (U.S. Environmental Protection Agency). 2000a. *Estimated Per Capita Fish Consumption in the United States: Based on Data Collected by the United States Department of Agriculture's 1994–1996 Continuing Survey of Food Intakes by Individuals*. Washington, DC: U.S. Environmental Protection Agency, Office of Science and Technology, Office of Water.

USEPA (U.S. Environmental Protection Agency). 2000b. *Methodology for Deriving Ambient Water Quality Criteria for the Protection of Human Health*. EPA-822-B-00-004. Washington, DC: U.S. Environmental Protection Agency, Office of Water. <http://www.epa.gov/waterscience/criteria/humanhealth/method/index.html>.

USEPA (U.S. Environmental Protection Agency). 2000c. *Guidance for Assessing Chemical Contaminant Data for Use in Fish Advisories*. Volume 1: Fish Sampling and Analysis, 3rd ed. EPA/823/B-00/007. Washington, DC: U.S. Environmental Protection Agency, Office of Water. <http://www.epa.gov/ost/fishadvice/volume1/index.html>

USEPA (U.S. Environmental Protection Agency). 2000d. *Quality Assurance Project Plan for Analytical Control and Assessment Activities in the National Study of Chemical Residues in Lake Fish Tissue.* EPA-823-R-02-006. Washington, DC: U.S. Environmental Protection Agency, Office of Water. < http://www.epa.gov/waterscience/fish/study/data/qaplan.pdf>

USEPA (U.S. Environmental Protection Agency). 2000e. *Guidance for the Data Quality Objectives Process*. EPA/600/R-96/055. Washington, DC: U.S. Environmental Protection Agency, Office of Environmental Information. <http://www.epa.gov/quality/qs-docs/g4-final.pdf>

USEPA (U.S. Environmental Protection Agency). 2000f. *Guidance for Assessing Chemical Contaminant Data for Use in Fish Advisories*. Volume 2: *Risk Assessment and Fish Consumption Limits*, 3rd ed. EPA/823/B-00/008. Washington, DC: U.S. Environmental Protection Agency, Office of Water. <http://www.epa.gov/ost/fishadvice/volume2/index.html>

USEPA (U.S. Environmental Protection Agency). 2000g. *Draft Florida Pilot Mercury Total Maximum Daily Load (TMDL) Study: Application of the Everglades Mercury Cycling Model (E-MCM) to Site WCA 3A-15*. Prepared for the U.S. Environmental Protection Agency and Florida Department of Environmental Protection. Lafayaette, California: Tetra Tech, Inc.

USEPA (U.S. Environmental Protection Agency). 2000h. *Deposition of Air Pollutants to the Great Waters: Third Report to Congress*. EPA-453/R-00-005. Research Triangle Park, NC: U.S. Environmental Protection Agency, Office of Air Quality Planning and Standards. <http://www.epa.gov/oar/oaqps/gr8water/3rdrpt>

USEPA (U.S. Environmental Protection Agency). 2000i. *AQUATOX*. EPA Release 1. File Version 1.69. EPA-823-B-00-007. Washington, DC: U.S. Environmental Protection Agency, Office of Water. <http://www.epa.gov/waterscience/models/aquatox/technical/techdoc.pdf>

USEPA (U.S. Environmental Protection Agency). 2000j. *Use of Fish and Shellfish Advisories and Classifications in 303(d) and 305(b) Listing Decisions*. Washington, DC: U.S. Environmental Protection Agency, Office of Science and Technology and Office of Wetlands, Oceans, and Watersheds. <http://www.epa.gov/waterscience/library/wqstandards/shellfish.pdf>

USEPA (U.S. Environmental Protection Agency). 2001a. *Water Quality Criterion for the Protection of Human Health: Methylmercury*. EPA-823-R-01-001. Washington, DC: U.S. Environmental Protection Agency, Office of Water. <http://www.epa.gov/waterscience/criteria/methylmercury/document.html>

USEPA (U.S. Environmental Protection Agency). 2001b. *Mercury Maps: A Quantitative Spatial Link Between Air Deposition and Fish Tissue*. Peer-reviewed final report. EPA-823-R-01-009. Washington, DC: U.S. Environmental Protection Agency, Office of Water. <http://www.epa.gov/waterscience/maps/report.pdf>

USEPA (U.S. Environmental Protection Agency). 2001c. Water quality criteria: Notice of Availability of water quality criterion for the protection of human health: Methylmercury. *Fed. Regist*., 66:1344. Washington, DC: U.S. Environmental Protection Agency, Office of Water. <http://www.epa.gov/fedrgstr/EPA-WATER/2001/January/Day-08/w217.htm>

USEPA (U.S. Environmental Protection Agency). 2001d. Draft Method 1630. *Methyl Mercury in Water by Distillation, Aqueous Ethylation, Purge and Trap, and CVAFS*. EPA-821-R-01-020. Washington, DC: U.S. Environmental Protection Agency.

USEPA (U.S. Environmental Protection Agency). 2001e. *Survey of Chemical Contaminants in Fish, Invertebrates and Plants Collected in the Vicinity of Tyonek, Seldovia, Port Graham and Nanwalek—Cook Inlet, Alaska*. Draft. EPA 910-R-01-003. Seattle, Washington: U.S. Environmental Protection Agency, Region 10.

USEPA (U.S. Environmental Protection Agency). 2001f. *Total Maximum Daily Load for Total Mercury in the Middle/Lower Savannah River, GA*. Atlanta, Georgia: U.S. Environmental Protection Agency, Region 4. <http://www.epa.gov/owow/tmdl/examples/mercury.html>

USEPA (U.S. Environmental Protection Agency). 2001g. Draft. *Results of Lake Michigan Mass Balance Study: Mercury Data Report*. EPA 905-R-01-012. Chicago, Illinois: U.S. Environmental Protection Agency, Great Lakes National Program Office.

USEPA (U.S. Environmental Protection Agency). 2001h. *Robust Estimation of Mean and Variance Using Environmental Data Sets with Below Detection Limit Observations*. Las Vegas, Nevada: U.S. Environmental Protection Agency, Office of Research and Development. <http://www.epa.gov/esd/cmb/research/papers/jn103.pdf>

USEPA (U.S. Environmental Protection Agency). 2001i. *Mercury TMDLs for Subsegments Within Mermentau and Vermillion-Teche River Basins*. Dallas, Texas: U.S. Environmental Protection Agency, Region 6. <http://www.epa.gov/region6/water/ecopro/latmdl/mercurytmdls_f.pdf>

USEPA (U.S. Environmental Protection Agency). 2001j. *Mercury TMDLs for Subsegments within Mermentau and Vermillion-Teche River Basins*. U.S. Environmental Protection Agency, Region 6, Watershed Management Section, Water Quality Protection Division, with cooperation from Louisiana Department of Environmental Quality, Office of Environmental Assessment, Environmental Technology Division. Dallas, Texas: U.S. Environmental Protection Agency, Region 6. <http://www.epa.gov/region6/water/tmdl.htm>

USEPA (U.S. Environmental Protection Agency). 2002a. *Integrated Risk Information System (IRIS). Methylmercury*. Oral RfD and inhalation RfC assessments last revised 7/27/2001. Carcinogenicity assessment last revised 5/1/1995. U.S. Environmental Protection Agency, Office of Research and Development, National Center for Environmental Assessment. <http://www.epa.gov/iris/subst/0073.htm>

USEPA (U.S. Environmental Protection Agency). 2002b. *Estimated Per Capital Fish Consumption in the United States*. EPA-821-C-02-003. Washington, DC: U.S. Environmental Protection Agency, Office of Water. <http://www.epa.gov/waterscience/fish/consumption_report.pdf>

USEPA (U.S. Environmental Protection Agency). 2002c. Method 1631. M*ercury in Water by Oxidation, Purge and Trap, and Cold Vapor Atomic Fluorescence Spectrometry*. EPA-821-R-02-019. Washington, DC: U.S. Environmental Protection Agency.

USEPA (U.S. Environmental Protection Agency). 2002d. *Guidance on Choosing a Sampling Design for Environmental Data Collection, for Use in Developing a Quality Assurance Project Plan.* EPA QA/G-5S. EPA/240/R-02/005. Washington, DC: U.S. Environmental Protection Agency, Office of Environmental Information, December 2002. <http://www.epa.gov/quality/qs-docs/g5s-final.pdf>.

USEPA (U.S. Environmental Protection Agency). 2002e. *Consolidated Assessment and Listing Methodology, Toward a Compendium of Best Practices,* 1st ed. Washington, DC: U.S. Environmental Protection Agency, Office of Wetlands, Oceans and Watersheds. <http://www.epa.gov/owow/monitoring/calm.html>

USEPA (U.S. Environmental Protection Agency). 2002f. *Review of 2002 Section 303(d) Lists and Guidelines for Reviewing TMDLs under Existing Regulations issued in 1992*. Memorandum from Charles Sutfin, May 20, 2002. Washington, DC: U.S. Environmental Protection Agency, Office of Wetlands, Oceans and Watersheds.<http://www.epa.gov/owow/tmdl/guidance/csmemo.html>.

USEPA (U.S. Environmental Protection Agency). 2002g. *National Sediment Quality Survey Database, 1980–1999*. Washington, DC: U.S. Environmental Protection Agency, Office of Water. <http://www.epa.gov/waterscience/cs/library/nsidbase.html>

USEPA (U.S. Environmental Protection Agency). 2003. *Methodology for deriving ambient water quality criteria for the protection of human health* (2000). Technical Support Document vol. 2, *Development of National Bioaccumulation Factors.* EPA-822-R-03-030. Washington, DC: U.S. Environmental Protection Agency, Office of Water. <http://www.epa.gov/waterscience/humanhealth/method/tsdvol2.pdf>

USEPA (U.S. Environmental Protection Agency). 2004. *Local Limits Development Guidance*. EPA-833-R-04-002A. U.S. Environmental Protection Agency, Office of Wastewater Management. July 2004. <http://www.epa.gov/npdes/pubs/final_local_limits_guidance.pdf >

USEPA (U.S. Environmental Protection Agency). 2005a. *Regulatory Impact Analysis of the Clean Air Mercury Rule*. Final report. EPA-452/R-05-003. Research Triangle Park, NC: U.S. Environmental Protection Agency, Office of Air Quality Planning and Standards, Air Quality Strategies and Standards Division. <http://www.epa.gov/ttn/atw/utility/ria_final.pdf>[25]

USEPA (U.S. Environmental Protection Agency). 2005b. *Environmental Monitoring and Assessment Project (EMAP) Western Streams and Rivers Statistical Study*. EPA-620-R-05-006. Washington, DC: U.S. Environmental Protection Agency, Office of Research and Development.

USEPA (U.S. Environmental Protection Agency). 2005c. *Technical Support Document, Revision of December 2000 Regulatory Finding on the Emissions of Hazardous Air Pollutants From Electric Utility Steam Generating Units and the Removal of Coal- and Oil-Fired Electric Utility Steam Generating Units from the Section 112(c) List: Reconsideration, October 21, 2005*.

USEPA (U.S. Environmental Protection Agency). 2005d. *Technical Support Document for the Final Clean Air Mercury Rule: Air Quality Modeling*. Research Triangle Park, NC: U.S. Environmental Protection Agency, Office of Air Quality Planning and Standards. <http://www.epa.gov/ttn/atw/utility/aqm_oar-2002-0056-6130.pdf>[26]

USEPA (U.S. Environmental Protection Agency). 2005e. Method 245.7, Revision 2.0. *Mercury in Water by Cold Vapor Atomic Fluorescence Spectrometry*. EPA-821-R-05-001. Washington, DC: U.S. Environmental Protection Agency.

USEPA (U.S. Environmental Protection Agency). 2005f. *Standards of Performance for New and Existing Stationary Sources: Electric Utility Steam Generating Units*. U.S. Environmental Protection Agency. *Fed. Regist.*, May 18, 2005, 70:28606.

USEPA (U.S. Environmental Protection Agency). 2005g. Method 245.7, Revision 2.0. *Mercury in Water by Cold Vapor Atomic Fluorescence Spectrometry*. EPA-821-R-05-001. Washington, DC: U.S. Environmental Protection Agency.

USEPA (U.S. Environmental Protection Agency). 2005h. Presentation for the Meeting with National Mining Association, Robert J. Wayland, Ph.D., Office of Air Quality Planning and Standards, September 28, 2005. EPA-HQ-OAR-2002-0056-6447.

USEPA (U.S. Environmental Protection Agency). 2007. *Listing Waters Impaired by Atmospheric Mercury Under Clean Water Act Section 303(d): Voluntary Subcategory 5m for States with Comprehensive Mercury Reduction Programs*, Craig Hooks, March 8, 2007. <http://www.epa.gov/owow/tmdl/mercury5m/>

[25] On February 8, 2008, the D.C. Circuit Court of Appeals vacated the Clean Air Mercury Rule and remanded portions of it to EPA, for reasons unrelated to the technical analyses in this document.

[26] On February 8, 2008, the D.C. Circuit Court of Appeals vacated the Clean Air Mercury Rule and remanded portions of it to EPA, for reasons unrelated to the technical analyses in this document.

USEPA (U.S. Environmental Protection Agency). 2008a. *Elements of Mercury TMDLs Where Mercury Loadings Are Predominantly from Air Deposition*, Craig E. Hooks, September 29, 2008. <http://epa.gov/owow/tmdl/guidance.html#1> at <http://www.epa.gov/owow/tmdl/pdf/cover_memo_mercury_tmdl_elements.pdf> and <http://www.epa.gov/owow/tmdl/pdf/document_mercury_tmdl_elements.pdf>

USEPA (U.S. Environmental Protection Agency). 2008b. *EPA's 2008 Report on the Environment.* EPA 600-R-07-045F. Washington, DC: U.S. Environmental Protection Agency. http://www.epa.gov/roe/downloads.htm and http://cfpub.epa.gov/eroe/index.cfm?fuseaction=detail.viewMidImg&lShowInd=0&subtop=341&lv=list.listByAlpha&r=216615#11215 (last updated April 13, 2010.

USEPA (U.S. Environmental Protection Agency). 2009a. *2008 Biennial National Listing of Fish Advisories*. EPA 823-F-09-007. Washington, DC: U.S. Environmental Protection Agency, Office of Water. http://www.epa.gov/waterscience/fish/advisories/tech2008.pdf>

USEPA (U.S. Environmental Protection Agency). 2009b. *The National Study of Chemical Residues in Lake Fish Tissue. EPA 823-R-09-006.* Washington, DC: U.S. Environmental Protection Agency, Office of Water. http://www.epa.gov/waterscience/fish/study/data/finalreport.pdf

Voiland, M.P., K.L. Gall, D.J. Lisk, and D.B. MacNeill. 1991. Effectiveness of recommended fat-trimming procedures on the reduction of PCB and Mirex levels in Brown trout (*Salmo trutta*) from Lake Ontario. *J. Great Lakes Res*. 17(4):454–460.

Wagemann, R., E. Trebacz, R. Hunt, and G. Boila. 1997. Percent methylmercury and organic mercury in tissues of marine mammals and fish using different experimental and calculation methods. *Environ. Toxicol. Chem*. 16(9):1859–1866.

Watras, C.J., R.C. Back, S. Halvorsen, R.J.M. Hudson, K.A. Morrison, and S.P. Wente. 1998. Bioaccumulation of mercury in pelagic freshwater food webs. *Sci. Total Environ.* 219(2–3):183–208.

Watras, C.J. and N.S. Bloom. 1992. Mercury and methylmercury in individual zooplankton: Implications for bioaccumulation. *Limnol. Oceanogr.* 37:1313–1318.

Watras, C.J., K.A. Morrison, J.S. Host, and N.S. Bloom. 1995. Concentration of mercury species in relationship to other site-specific factors in the surface waters of northern Wisconsin lakes. *Limnol. Oceanogr.* 40:556–565.

Wente, S.P. 2003. A Spatially and Temporally Variable Model of Mercury Concentrations in Aquatic Communities with Applications to Public Health Protection and Water Quality Assessment. Ph.D. thesis, Purdue University, West Lafayette, Indiana.

Wente, S.P. 2004. *A Statistical Model and National Data Set for Partitioning Fish-Tissue Mercury Concentration Variation Between Spatiotemporal and Sample Characteristic Effects*. Scientific Investigation Report 2004-5199. Reston, Virginia: U.S. Geological Survey.

WLSSD (Western Lake Superior Sanitary District). 1997. *The WLSSD Commitment to Zero Discharge*. Duluth, MN: Western Lake Superior Sanitary District. <http://www.wlssd.duluth.mn.us/Zero_Discharge_Com.pdf.pdf>

Wren, C.D. and H.R. MacCrimmon. 1986. Comparative bioaccumulation of mercury in two adjacent freshwater ecosystems. *Water Res.* 6:763-769.

Yantosca, B. 2004. *GEOS-CHEMv7-01-02 User's Guide*. Cambridge, MA: Atmospheric Chemistry Modeling Group, Harvard University.

Appendix A. Methylmercury/Mercury Ratio Exhibited in Muscle Tissue of Various Freshwater Fish Species

Source	Ecosystem type	Fish species	MethylHg/ total Hg ratio
Hammerschmidt et al. 1999	Freshwater lakes in Wisconsin, USA	Yellow perch (*Perca flavescens*)	mean: 0.95 range: 0.84 to 0.97
Becker and Bigham 1995	Onondaga Lake, a chemically contaminated lake in New York, USA	Gizzard shad (*Dorosoma cepedianum*) White perch (*Morone americana*) Carp (*Cyprinus carpio*) Channel catfish (*Ictalurus punctatus*) Bluegill (*Lepomis macrochirus*) Smallmouth bass (*Micropterus dolomieui*) Walleye (*Stizostedion vitreum*)	> 0.90 Note: Authors did not provide specific percentages for individual species.
Grieb et al. 1990	Lakes in the Upper Michigan Peninsula, USA	Yellow perch (*Perca flavescens*) Northern pike (*Esox lucius*) Largemouth bass (*Micropterus salmoides*) White sucker (*Catostomus commersoni*)	0.99 Note: Authors did not provide data for each species separately—only mean value observed over all species.
Bloom 1992	Freshwater fish species collected from remote midwestern lakes and one mercury contaminated site USA	Yellow perch (*Perca flavescens*) Northern pike (*Esox lucius*) White sucker (*Catostomus commersoni*) Largemouth bass (*Micropterus salmoides*)	0.99 1.03 0.96 0.99
Lasorsa and Allen-Gil 1995	3 lakes in the Alaskan Arctic, USA	Arctic grayling Lake trout Arctic char Whitefish	1.00 all for species Note: Authors did not provide species-specific information on MeHg/total Hg ratio.
Kannan, et al. 1998	Estuaries in South Florida	Hardhead catfish (*Arius felis*) White grunt (*Haemulon plumieri*) Sand perch (*Diplectrum formosum*), Lane snapper (*Lutjanus synagris*) Gafftopsail catfish (*Bagre marinus*) Pinfish (*Lagodon rhomboides*) Spot (*Leiostomus xanthurus*) Pigfish (*Orthopristis chrysoptera*) Sand seatrout (*Cynoscion arenarius*) Brown shrimp (*Penaeus aztecus*)	0.90 0.91 0.91 0.97 0.71 0.78 0.75 0.82 0.85 0.72 Note: Author sampled the 10 fish species at 20 locations.
Jackson 1991	Lakes and reservoirs in northern Manitoba, Canada	Walleye (*Stizostedion vitreum*) Northern pike (*Esox lucius*) Lake whitefish (*Coregonus clupeaformis*)	range: 0.806% to 0.877% range: 0.824% to 0.899% range: 0.781% to 0.923% Note: Author sampled the 3 fish species at 4 lake locations.

Source	Ecosystem type	Fish species	MethylHg/ total Hg ratio
Wagemann et al. 1997	Sampling location not provided; presumed to be from Canadian waters	Walleye (*Stizostedion vitreum*)	mean 1.00 Note: Authors did not provide more specific information.

For trophic level assignments for specific fish species, refer to tables 6-4 and 6-6 of the 2000 Human Health BAF guidance (USEPA 2003). Additional information on trophic level assignments is in the appendix of that guidance (http://www.epa.gov/waterscience/criteria/humanhealth/method/tsdvol2.pdf).

Appendix B. Tables from Methylmercury Criteria Document

This appendix contains several tables taken directly from the 2001 methylmercury criteria document. They are repeated here to help the reader understand the development of the 2001 criterion.

Table B1. Exposure parameters used in derivation of the water quality criterion.

(References cited in this table can be found in the 2001 methylmercury criterion document.)

Parameter	Population			Source
	Children (0-14 years)	Women of Childbearing Age (15-44 years)	Adults in the General Population	
Body Weight, kg	30	67	70	USEPA (2000f)
Drinking Water Intake, L/day	1.0	2.0	2.0	USEPA (2000f)
Freshwater/Estuarine Fish Intake, g/day	156.3[a]	165.5[a]	17.5[b,c]	USEPA (2000f)
Inhalation, m^3/day	10.4	11	20	USEPA (1994, 1997d)[d]
Soil Ingestion, g/day	0.0001, 0.01[e]	0.00005	0.00005	USEPA (1997d)
Mean Marine Fish Intake, g/day	74.9[a]	91.04[a]	12.46[b]	USEPA (2000a)
Median Marine Fish intake, g/day	59.71[a]	75.48[a]	0[b]	USEPA (2000a)
90th Percentile Marine Fish Intake, g/day	152.29[a]	188.35[a]	49.16[b]	USEPA (2000a)

Notes:

[a] For children and women of childbearing age, intake rates are estimates of "consumers only" data (as described in USEPA 2000a).

[b] For adults in the general population, intake rates are estimates of all survey respondents to derive an estimate of long-term consumption (USEPA).

[c] This is the 90th percentile freshwater and estuarine fish consumption value.

[d] Inhalation rates for children and women of childbearing age from USEPA, 1997d. Inhalation rates for adults in the general population from USEPA (1994).

[e] Pica child soil ingestion.

Table B2. Average mercury concentrations in marine fish and shellfish[a]

(References cited in this table can be found in the 2001 methylmercury criteria document.)

Species	Concentration[b] (µg Hg/g Wet Wt.)	Species	Concentration (µg Hg/g Wet Wt.)
Finfish			
Anchovy	0.047	Pompano*	0.104
Barracuda, Pacific	0.177	Porgy*	0.522[d]
Cod*	0.121	Ray	0.176
Croaker, Atlantic	0.125	Salmon*	0.035
Eel, American	0.213	Sardines*	0.1
Flounder*[,c]	0.092	Sea Bass*	0.135
Haddock*	0.089	Shark*	1.327
Hake	0.145	Skate	0.176
Halibut*	0.25	Smelt, Rainbow*	0.1
Herring	0.013	Snapper*	0.25
Kingfish	0.10	Sturgeon	0.235
Mackerel*	0.081	Swordfish*	0.95[e]
Mullet	0.009	Tuna*	0.206
Ocean Perch*	0.116	Whiting (silver hake)*	0.041
Pollock*	0.15	Whitefish*	0.054[f]
Shellfish			
Abalone	0.016	Oysters	0.023
Clam*	0.023	Scallop*	0.042
Crab*	0.117	Shrimp	0.047
Lobster	0.232	Other shellfish*	0.012[d]
Molluscan Cephalopods			
Octopus*	0.029	Squid*	0.026

Notes:

*Denotes species used in calculation of methylmercury intake from marine fish for one or more populations of concern, based on existence of data for consumption in the CSFII (USEPA 2000a).

[a] More current information on commercial fish and shellfish is provided by the Food and Drug Administration at http://www.cfsan.fda.gov/%7Efrf/sea-mehg.html.

[b] Mercury concentrations are from NOAA (1978) as referenced in the NMFS database, as reported in USEPA (1997c) unless otherwise noted, measured as micrograms (µg) of mercury per gram (g) wet weight of fish tissue.

[c] Mercury data for flounder were used to estimate mercury concentration in marine flatfish for intake calculations.

[d] Mercury concentration data are from Stern et al. (1996) as cited in USEPA (1997f).

[e] Mercury concentration data are from U.S. FDA Compliance Testing as cited in USEPA (1997f).

[f] Mercury concentration data are from U.S. FDA (1978) compliance testing as described in the NMFS database, as cited in USEPA (1997f).

Table B3. Exposure estimates for methylmercury and percent of total exposure based on adults in the general population

Exposure Source	Exposure Estimate (mg/kg-day)	Percent of Total Exposure	Percent of RfD
Ambient water intake	4.3×10^{-9}	0.0047	0.004
Drinking water intake[a]	5.6×10^{-8}	0.0605	0.006
Nonfish dietary intake	0	0	0
Marine fish intake	2.7×10^{-5}	29.33	27
Air intake	4.6×10^{-9}	0.005	0.005
Soil intake	1.3×10^{-9}	0.0014	0.001

Note:

[a] This represents the high-end of the range of estimates. Because the contribution of ambient water or drinking water intake to total exposure is so negligible in comparison to the sum of intake from other sources, there is not difference in the total exposure estimated using either of these two alternatives.

Appendix C. Analytical Methods

Table C1. Analytical methods for determining mercury and methylmercury in tissue

Method	Form/species and applicable matrices	Quantitation Level or ML[a]	Technique	Known studies or literature references using the techniques in this method
Method 1630, with draft modifications for tissue (Recommended method – see section 4.1.3)	Methylmercury in tissue	0.001 mg/kg 0.002 mg/kg	Tissue modification: digest tissue with acid solution, neutralize with acetate buffer, and analyze as per Method 1630, i.e., distillation with heat and N_2 flow to separate methylHg from sample, ethylation with sodium tetraethyl borate, N_2 purging of methylethylHg onto graphite carbon (Carbotrap) column, thermal desorption of methylethylHg and reduction to Hg^0, followed by CVAFS detection.	• EPA Cook Inlet Contaminant Study • Lake Michigan fish and invertebrates, Mason and Sullivan 1997 • Northeastern Minnesota lake plankton, Monson and Brezonik 1998[b] • Method performance testing in freshwater and marine fish, Bloom 1989
Method 1631, draft appendix A (Recommended method – see section 4.1.3)	Total mercury in tissue, sludge, and sediment	0.002 mg/kg	Digest tissue with HNO_3/H_2SO_4. Dilute digestate with BrCl solution to destroy remaining organic material. Analyze digestate per method 1631: Add BrCl to oxidize all Hg compounds to Hg(II). Sequentially pre-reduced with hydroxylamine hydrochloride to destroy the free halogens and reduced with $SnCl_2$ to convert Hg(II) to Hg(0). Hg(0) is purged from solution onto gold-coated sand trap and thermally desorbed from trap for detection by CVAFS.	• EPA National Fish Tissue Study (>1,000 samples over 4-year period) • EPA Cook Inlet Contaminant Study • Lake Michigan fish and invertebrates, Mason and Sullivan 1997 • Northeastern Minnesota lake plankton, Monson and Brezonik 1998[b] • Method performance testing in freshwater and marine fish, Bloom 1989
Method 245.6	Total mercury in tissue	0.020 mg/kg	Sulfuric and nitric acid digestion, oxidation with potassium permanganate and potassium persulfate, $SnCl_2$ reduction, CVAAS detection	Unknown
Draft method 7474 (SW-846)	Total mercury in sediment and tissue	40 mg/kg	Microwave digestion of sample in nitric and hydrochloric acids, followed by cold digestion with bromate/bromide in HCl. Hg purged from sample and determined by CVAFS.	Reference materials cited in method. Niessen et al. 1999.

Notes:

[a] Quantitation level or minimum level (ML) is considered the lowest concentration at which a particular contaminant can be quantitatively measured using a specified laboratory procedure for monitoring of the contaminant.

[b] Used similar techniques but used a methylene chloride extraction instead of the distillation.

Table C2. Analytical methods for determining mercury and methylmercury in water, sediment, and other nontissue matrices

Method	Forms/species and applicable matrices	Quantitation Level or ML	Sample preparation	Known studies or literature references using the techniques in this method
EPA 1630[a] (Recommended method – see section 4.1.3)	Methylmercury in water	0.06 ng/L	Distillation with heat and N_2 flow, addition of acetate buffer and ethylation with sodium tetraethyl borate. Purge with N_2 onto Carbotrap. Thermal desorption and GC separation of ethylated mercury species, reduction to Hg^0 followed by CVAFS detection.	• USEPA Cook Inlet Study • USEPA Savannah River TMDL study • Northern Wisconsin Lakes, Watras et al. 1995 • Lake Michigan waters, Mason and Sullivan 1997 • Anacostia River Study, Mason and Sullivan 1998 • Northeastern Minnesota lakes, Monson and Brezonik 1998[b] • Poplar Creek, TN CERCLA Remedial Investigation of surface water, sediment, and pore water, Cambell et al. 1998[c] • Scheldt estuary study of water, polychaetes, and sediments, Baeyens et al. 1998
UW-Madison SOP for MeHg Analysis[a]	Methylmercury in water	0.01 ng/L	Distillation with heat and N_2 flow, with potassium chloride, sulfuric acid, and copper sulfate. Ethylation with sodium tetraethyl borate. Purge with N_2 onto Carbotrap. Thermal desorption and GC separation of ethylated mercury species, reduction to Hg^0 followed by CVAFS detection.	• Lake Michigan tributaries to support GLNPO's LMMB Study • Fox River, WI, waters and sediments, Hurley et al. 1998
USGS Wisconsin - Mercury Lab SOPs 004[a]	Methylmercury in water	0.05 ng/L	Distillation (heat), APDC solution, N_2 flow, potassium chloride, sulfuric acid, and copper sulfate. Ethylation with sodium tetraethyl borate. Purge with N_2 onto Carbotrap. Thermal desorption and GC separation of ethylated species, reduction to Hg^0, and CVAFS detection.	Aquatic Cycling of Mercury in the Everglades (ACME). cofunded by USGS, EPA, and others
USGS Open-File Report 01-445[a]	Methylmercury in water	0.04 ng/L	Distillation (heat) and N_2 flow, HCl and copper sulfate. Addition of acetate buffer and ethylation with sodium tetraethyl borate. Purge with N_2 onto Carbotrap. Thermal desorption and GC separation of ethylated mercury species, reduction to Hg(0) followed by CVAFS detection.	Formalized USGS method version of USGS Wisconsin Lab SOP 004. Report title is Determination of Methyl Mercury by Aqueous Phase Ethylation, Followed by GC Separation with CVAFS Detection.

Table C2. Analytical methods for determining mercury and methylmercury in water, sediment, and other nontissue matrices *(continued)*

Method	Forms/species and applicable matrices	Quantitation Level or ML	Sample preparation	Known studies or literature references using the techniques in this method
EPA 1631, revision E[d] (CVAFS) (Recommended method – see section 4.1.3)	Total or dissolved mercury in water	ML = 0.5 ng/L (MDL = 0.2 ng/L)	Oxidize all Hg compounds to Hg(II) with BrCl. Sequentially pre-reduce with hydroxylamine hydrochloride to destroy the free halogens and reduce with $SnCl_2$ to convert Hg(II) to Hg(0). Hg(0) is purged from solution with N_2 onto gold coated sand trap and thermally desorbed from trap for detection by CVAFS.	• USEPA Cook Inlet Study • State of Maine studies • USEPA Savannah River TMDL study • USEPA/U.S. Navy study for development of Uniform National Discharge Standards • Watras et al. 1995 • Anacostia River Study, Mason and Sullivan 1998 • Northeastern Minnesota lakes, Monson and Brezonik 1998 • Poplar Creek, TN, CERCLA Remedial Investigation Study, Cambell et al. 1998 • Scheldt Estuary Study, Baeyens et al. 1998
EPA 245.1[d] (CVAAS)	Total or dissolved mercury in wastewater	200 ng/L	H_2SO_4 and HNO_3 digestion, $KMnO_4$, $K_2S_2O_8$ oxidation + heat, cool +NaCl-$(NH_2OH)_2{\cdot}H_2SO_4$, $SnSO_4$, aeration. Detection by CVAAS.	Effluent guideline development studies for the Meat Products Industry, Metal Products and Machinery Industry, and Waste Incinerators
EPA 245.2[d] (CVAAS)	Total or dissolved mercury in wastewater and sewage	200 ng/L	H_2SO_4 and HNO_3 added, $SnSO_4$, NaCl-$(NH_2OH)_2{\cdot}H_2SO_4$, $KMnO_4$, $K_2S_2O_8$, heat. Detection by CVAAS.	MPM Industry effluent guideline development study
EPA 245.5 (CVAAS)	Total or dissolved mercury in soils, sludge and sediment	200 ng/L	Dry sample, aqua regia, heat, $KMnO_4$ added, cool +NaCl-$(NH_2OH)_2{\cdot}H_2SO_4$, $SnSO_4$, aeration. Detection by CVAAS.	Pharmaceutical industry effluent guideline development study
EPA 245.7[d] (CVAFS) (Recommended method – see section 4.1.3)	Total or dissolved mercury in water	ML = 5 ng/L; (MDL = 1.8 ng/L) [e]	HCl, $KBrO_3$ /KBr, $NH_2OH{\cdot}HCl$, $SnCl_2$, liquid-vapor separation. CVAFS detection	Interlaboratory validation completed
EPA 7470A (CVAAS)	Total or dissolved mercury in liquid wastes and ground water	200 ng/L (IDL)	H_2SO_4 and HNO_3 added, $KMnO_4$ added, $K_2S_2O_8$ added + heat, cool +NaCl-$(NH_2OH)_2{\cdot}H_2SO_4$, $SnSO_4$, aeration of sample. CVAAS detection.	Method is similar to and cites performance data given in EPA 245.5.

Table C2. Analytical methods for determining mercury and methylmercury in water, sediment, and other nontissue matrices *(continued)*

Method	Forms/species and applicable matrices	Quantitation Level of ML	Sample preparation	Known studies or literature references using the techniques in this method
EPA 7471B (CVAAS)	Total or dissolved mercury in solid wastes and semisolid wastes	200 ng/L (IDL)	H_2SO_4 and HNO_3 added, $KMnO_4$ added, $K_2S_2O_8$ added + heat, cool +NaCl-$(NH_2OH)_2{\cdot}H_2SO_4$, $SnSO_4$, aeration of sample. CVAAS detection.	Method is similar to and cites performance data given in EPA 245.5.
EPA 7472 (Anodic stripping voltametry)	Total or dissolved mercury in water	100-300 ng/L	Acidify and chlorinate sample, GCE electrode	Unknown
EPA 7473 (Thermal decomposition, amalgamation, and CVAA)	Mercury in water, soil, and sediment	estimated to be as low as 20 ng/ L or 20 ng/kg	Sample aliquot decomposed at 750°C in oxygen atmosphere. Decomposition products carried into catalytical furnace for completed oxidations, then to algamated trap. Mercury is thermally desorbed and determined by CVAA.	Unknown
Draft Method 7474 (SW-846)[f]	Total mercury in sediment and tissue	20 ng/g	Microwave digestion of sample in nitric and hydrochloric acids, followed by cold digestion with bromate/bromide in HCl. Hg purged from sample and determined by CVAFS.	Reference materials cited in method. Niessen et al. 1999.
EPA 1620 (CVAAS)	Mercury in water, sludge, and soil	200 ng/L	H_2SO_4 and HNO_3 added, $KMnO_4$, $K_2S_2O_8$ + heat, cool +NaCl-$(NH_2OH)_2{\cdot}H_2SO_4$, $SnSO_4$, aeration. CVAAS detection.	Industry effluent guideline development studies
SM 3112B (CVAAS)	Total or dissolved mercury in water	500 ng/L	H_2SO_4 and HNO_3 added, $KMnO_4$ added, $K_2S_2O_8$ added + heat, cool +NaCl $(NH_2OH)_2{\cdot}H_2SO_4$, $SnCl_2$ or $SnSO_4$, aeration. CVAAS determination.	Unknown
ASTM D3223-97, 02 (CVAAS)	Total or dissolved mercury in water	500 ng/L	H_2SO_4 and HNO_3 added, $KMnO_4$ added,$K_2S_2O_8$ added + heat, cool +NaCl $(NH_2OH)_2{\cdot}H_2SO_4$, $SnSO_4$, aeration. CVAAS determination.	Unknown
AOAC 977.22 (Atomic absorption spectrometry)	Total or dissolved mercury in water	200 ng/L	H_2SO_4 and HNO_3 added, $KMnO_4$ added, $K_2S_2O_8$ added + heat, cool +NaCl $(NH_2OH)_2{\cdot}H_2SO_4$, $SnSO_4$, aeration. Determine mercury by CVAA.	Unknown

Notes: (1) CVAAS = cold vapor atomic absorption spectrometry.

(2) CVAFS = cold-vapor atomic fluorescence spectrometry.

(3) ASTM and AOAC analytical methods are available from the respective organization.

[a] All four methylmercury methods above are based on the work of Bloom 1989, as modified by Horvat et al. 1993, and are virtually identical as a result.

[b] Used similar techniques but used a methylene chloride extraction instead of the distillation.

[c] Used similar techniques but omitted the distillation procedure.

[d] Promulgated and approved under 40 CFR part 136, Table 1B.

[e] The method detection level (MDL) is the minimum concentration of an analyte (substance) that can be measured and reported with a 99 percent confidence that the analyte concentration is greater than zero as determined by the procedure set forth in appendix B of 40 CFR part 136.

[f] Provided for reference purposes only. EPA recommends using method 1631 for analyzing mercury for water and fish tissue.

Appendix D. Synopsized Mercury TMDLs Developed or Approved by EPA

I. Ochlockonee Watershed, Georgia

II. Arivaca Lake, Arizona

III. McPhee and Narraguinnep Reservoirs, Colorado

IV. Clear Lake, California

V. Cache Creek, California

VI. Minnesota Statewide Mercury Total Maximum Daily Load

I. Ochlockonee Watershed, Georgia

Description of the Applicable Water Quality Standards

TMDLs are established to attain and maintain the applicable narrative and numerical water quality standards. The State of Georgia's *Rules and Regulations for Water Quality Control* do not include a numeric criterion for the protection of human health from methylmercury, but they do provide a narrative "free from toxics" water quality standard. Because mercury can cause toxicity in humans, Georgia has used a numeric "interpretation" of its narrative water quality standard for toxic substances to ensure that a TMDL will protect human health. The numeric interpretation of its narrative water quality standard is a concentration of no more than 0.3 mg/kg methylmercury in fish tissue. This numeric interpretation protects the "general population," which is the population that consumes 17.5 g/day or less of freshwater fish.

This approach is consistent with EPA's recommended water quality criterion for the protection of human health from methylmercury, described in the document *Water Quality Criterion for the Protection of Human Health: Methylmercury* (USEPA 2001a). The methodology uses a "weighted consumption" approach. When only trophic level 3 and 4 fish have been collected, the methodology assumes that 8 g/day (58.4 percent) of the total fish consumption is trophic level 3 fish (e.g., catfish and sunfish) and 5.7 g/day (41.6 percent) is trophic level 4 fish (e.g., largemouth bass). EPA collected site-specific data from the Ochlockonee River on ambient mercury in fish tissue and in the water column in the summer of 2000 and in March and April 2001 at two locations. Using a weighted consumption approach, site-specific fish tissue concentration data collected in the Ochlockonee River yields a weighted fish tissue concentration of 0.6 mg/kg, which is greater than the state's current applicable water quality criterion of 0.3 mg/kg. This was calculated as

Weighted fish tissue concentration = (avg. trophic 4 conc. x .416) + (avg. trophic 3 conc. x .584)

where:

average trophic level 3 concentration = 0.2 mg/kg
average trophic level 4 concentration = 1.0 mg/kg
weighted fish tissue concentration = 0.6 mg/kg

To establish the TMDL, EPA determined the maximum allowable concentration of mercury in the ambient water that will prevent accumulation of methylmercury in fish tissue above the applicable water quality standard, 0.3 mg/kg. To determine this concentration, EPA used the *Methodology for Deriving Ambient Water Quality Criteria for the Protection of Human Health* (USEPA 2000b). EPA also used the recommended national values from the *Methodology*, including the reference dose of 0.0001 mg/kg-day methylmercury, a standard average adult body weight of 70 kg, and the consumption rate for the general population of 17.5 g/day. For the other factors in the calculation, bioaccumulation and fraction of methylmercury, EPA used site-specific data from the Ochlockonee River collected in summer 2000 and March and April 2001. From this site-specific data, EPA determined a representative weighted BAF. The BAF was calculated

by taking the average calculated BAF from each of the two trophic levels. The BAF calculation also used 0.17 as the measured fraction of the total mercury as methylmercury. Using this approach, an allowable concentration of mercury in the ambient water of Ochlockonee River for the protection of human health is 1.6 ng/L. This concentration was calculated as

$$WQS = \frac{((\text{reference dose} - RSC) \times \text{body weight} \times \text{units conversion})}{(\text{consumption rate} \times \text{weighted BAF} \times \text{fraction MeHg})}$$

Where:

WQS = water quality standard = 1.6 ng/L
reference dose = 0.0001 mg/kg-day MeHg
RSC = relative source contribution from other fish species = 0.000027 mg/kg-day MeHg
body weight = 70 kg
units conversion = 1,000,000 mg/kg
consumption rate = 0.0175 kg/day fish
weighted bioaccumulation factor = 1,063,270 l/kg
fraction of the mercury as methylmercury = 0.17 as measured

Source Assessment

A TMDL evaluation must examine all known potential sources of the pollutant in the watershed, including point sources, nonpoint sources, and background levels. The source assessment was used as the basis of development of a model and the analysis of TMDL allocation options. This TMDL analysis includes contributions from point sources, nonpoint sources, and background levels. Sixteen water point sources in the Ochlockonee River watershed could have mercury in their discharges.

According to a review of the *Mercury Study Report to Congress* (USEPA 1997c), significant potential air emission sources include coal-fired power plants, waste incinerators, cement and lime kilns, smelters, and chlor-alkali factories. In the report, a national airshed model (RELMAP) was applied to the continental United States. This model provides a distribution of wet and dry deposition of mercury as a function of air emissions and global sources, and it was used to calculate wet and dry deposition rates for south Georgia.

The MDN includes a national database of weekly concentrations of mercury in precipitation and the seasonal and annual flux of mercury in wet deposition. EPA reviewed the MDN data for a sampling station near south Georgia. The MDN data were compared with the RELMAP deposition predictions and the MDN data were found to be substantially higher. Using the MDN data, the average annual wet deposition rate was determined to be 12.75 µg/square meter. The dry deposition rate was determined to be 6.375 µg/square meter on the basis of the RELMAP results.

Loading Capacity—Linking Water Quality and Pollutant Sources

The link between the fish tissue endpoint and the identified sources of mercury was the basis for the development of the TMDL. The linkage analysis helped estimate the total

assimilative capacity of the river and any needed load reductions. In this TMDL, models of watershed loading of mercury were combined with a model of mercury cycling and bioaccumulation in the water. This approach enabled a translation between the endpoint for the TMDL (expressed as a fish tissue concentration of mercury) and the mercury loads to the water. The loading capacity was then determined by the linkage analysis as a mercury loading rate that was consistent with meeting the endpoint fish tissue concentration.

Watershed-scale loading of water and sediment was simulated using the WCS. The complexity of this loading function model falls between that of a detailed simulation model (which attempts a mechanistic, time-dependent representation of pollutant load generation and transport) and simple export coefficient models (which do not represent temporal variability). The WCS provides a mechanistic, simplified simulation of precipitation-driven runoff and sediment delivery, yet it is intended to be applicable without calibration. Solids load, runoff, and ground water can then be used to estimate pollutant delivery to the receiving waterbody from the watershed. This estimate is based on pollutant concentrations in wet and dry deposition, processed by soils in the watershed and ultimately delivered to the receiving waterbody by runoff, erosion, and direct deposition. The WCS-calculated loads for each subbasin are shown in table D1.

Table D1. Annual average mercury load from each subbasin

Watershed	Total Hg load (mg)	Areal load (mg/ha)	Impervious area (mg/yr)	Sediment (mg/yr)	Runoff (mg/yr)	Deposition on water (mg/yr)
Barnett Creek	786098.4	25.6	116614.69	422879.88	177553.9	68850
Middle/Lower Ochlocklonee	307965.8	21.24	125771.73	89440.3	54786.29	37867.5
Tired Creek	827172.8	22.03	252386.89	317969.16	194751.7	61965
Lower Ochlockonee	359317.5	15.62	100125.11	130407.68	97802.16	30982.5
Little Ochlockonee	873773.4	19.89	140023.69	433136.75	219614.2	80898.75
Bridge Creek	454417.5	23.11	53496.45	261042.44	98468.66	41310
Upper/Middle Ochlockonee	627746.1	20.67	152881.42	254746.48	182250.7	37867.5
Upper Ochlockonee	766396.8	20.1	164465.44	320337	186825.6	94668.75

WASP5 (Ambrose et al. 1988) was chosen to simulate mercury fate in the Ochlockonee River. WASP5 is a general, dynamic mass balance framework for modeling contaminant fate and transport in surface waters. Environmental properties and chemical concentrations are modeled as spatially constant within segments. Each variable is advected and dispersed among water segments and exchanged with surficial benthic segments by diffusive mixing. Sorbed or particulate fractions can settle through water column segments and deposit to or erode from surficial benthic segments. Within the bed, dissolved variables can migrate downward or upward through percolation and pore water diffusion. Sorbed variables can migrate downward or upward through net sedimentation or erosion.

The toxics WASP model, TOXI5, combines a kinetic structure adapted from EXAMS2 with the WASP5 transport structure and simple sediment balance algorithms to predict dissolved and sorbed chemical concentrations in the bed and overlying waters. TOXI5 simulates the transport and transformation of chemicals as a neutral compound and up to four ionic species, as well as particulate material. Local equilibrium is assumed so that the distribution of the chemical among the species and phases is defined by distribution or partition coefficients. The predicted mercury concentrations are shown in table D2.

Table D2. Predicted mercury for annual average load and flow

Calculated concentrations	River reach					
	1	2	3	4	5	6
Total Hg: water column (ng/L)	6.33	5.84	5.55	5.76	5.65	5.17
Total Hg: sediment (ng/g)	7.05	9.07	9.81	8.17	7.63	6.97
Methyl Hg: water column (ng/L)	0.90	0.82	0.77	0.79	0.77	0.71

Allocations

To determine the total maximum load that can enter the Ochlockonee River, the current loading conditions were evaluated and the instream concentration was determined using the modeling approach described above. This allowed the development of a relationship between load and instream mercury concentrations. Using this developed relationship, the total maximum load could be determined. Because the water column mercury concentration response is linear with respect to changes in load, a proportion could be developed to calculate the total maximum mercury load from the watershed that would achieve the derived water quality target of 1.6 ng/L. The TMDL was calculated as the ratio of the water quality target to the highest segment concentration (1.6 ng/L divided by 6.3 ng/L) applied to the current annual average load of 5.00 kg/yr. This gave a TMDL load of 1.22 kg/yr mercury, which represents a 76 percent reduction from the current annual average load.

In a TMDL assessment, the total allowable load is divided and allocated to the various pollutant sources. The calculated allowable load of mercury that can come into the Ochlockonee River without exceeding the applicable water quality target of 1.6 ng/L is 1.22 kg/yr. Because EPA's assessment indicates that over 99 percent of the current loading of mercury is from atmospheric sources, 99 percent of the allowable load is assigned to the load allocation and 1 percent of the allowable load is assigned to the wasteload allocation. Therefore, the load allocation and the wasteload allocation for the Ochlockonee River are:

Load allocation (atmospheric sources) = 1.16 kilograms/year
Wasteload allocation (NPDES sources) = 0.06 kilograms/year

EPA estimates that atmospheric deposition contributes over 99 percent of current mercury loadings to the river; therefore, significant reductions in atmospheric deposition will be necessary if the applicable water quality standard is to be attained. On the basis of the total allowable load of 1.22 kg/year, a 76 percent reduction of mercury loading is needed to achieve the applicable water quality standard. EPA believes that an estimated

31 percent to 41 percent reduction in mercury deposition to the Ochlockonee River watershed can be achieved by 2010 through full implementation of existing CAA requirements. In addition, a number of activities to address remaining sources of mercury are planned or under way, and EPA expects that further reductions in mercury loadings will occur over time as a result of those activities. EPA is not able to estimate the reductions in mercury deposition to the Ochlockonee River watershed that will be achieved from future activities. As contemplated by CWA section 303(d)(1)(C), however, this TMDL quantifies the water quality problem facing the Ochlockonee River watershed and identifies the needed reductions in loadings from atmospheric deposition—by CAA initiatives or under other authorities—for the watershed to achieve applicable standards for mercury. In addition, as EPA collects additional data and information for the Ochlockonee River watershed and as new legal requirements are imposed under the CAA, EPA will continue to evaluate the effectiveness of regulatory and nonregulatory air programs in achieving the TMDL's water quality target.

The analysis of NPDES point sources in the watershed indicates that the cumulative loading of mercury from these facilities is less than 1 percent of the total estimated current loading. Even if this TMDL allocated none of the calculated allowable load to NPDES point sources (a wasteload allocation of zero), the waterbody would not attain the applicable water quality standards for mercury because of the very high mercury loadings from atmospheric deposition. At the same time, however, EPA recognizes that mercury is an environmentally persistent bioaccumulative toxic with detrimental effects on human fetuses even at minute quantities and that it should be eliminated from discharges to the extent practicable. Taking these two considerations into account, this TMDL provides a wasteload allocation applicable to all Georgia NPDES-permitted facilities in the watershed in the amount of 0.06 kg/year. The TMDL was written so that all NPDES-permitted facilities will achieve this wasteload allocation by discharging mercury only at concentrations below the applicable water quality standard, 1.6 ng/L, or by implementing a pollutant minimization program.

In the context of this TMDL, EPA believes it can reasonably offer the choice of the two approaches to the permitting authority for the following reasons. First, on the basis of EPA's analysis, the Agency expects either wasteload allocation option, in the aggregate, to result in point source mercury loadings lower than the wasteload allocation. Second, EPA believes this flexibility is the best way of ensuring that the necessary load reductions are achieved without causing significant social and economic disruption. EPA recognizes that NPDES point sources contribute a small share of the mercury contributions to the Ochlockonee River. EPA also recognizes, however, that mercury is a highly persistent toxic pollutant that can bioaccumulate in fish tissue at levels harmful to human health. Therefore, EPA has determined, as a matter of policy, that NPDES point sources known to discharge mercury at levels above the amount present in their source water should reduce their loadings of mercury using appropriate, cost-effective mercury minimization measures to ensure that the total point source discharges are at a level equal to or less than the wasteload allocation specified in this TMDL. The point sources' waste load allocation will be applied to the increment of mercury in their discharge that is above the amount of mercury in their source water. EPA recommends that the permitting authority make this choice between the two options in consultation with the affected dischargers

because EPA is not able to make the case-by-case judgments in this TMDL that EPA believes are appropriate.

II. Arivaca Lake, Arizona

Description of the Applicable Water Quality Standards

Authorities develop TMDLs to meet applicable water quality standards. These standards may include numeric water quality standards, narrative standards describing designated uses, and other associated indicators supporting designated uses (beneficial uses apply only to California). A numeric target identifies the specific goals or endpoints for the TMDL that equate to attainment of the water quality standard. The numeric target may be equivalent to a numeric water quality standard (where one exists), or it may represent a quantitative interpretation of a narrative standard.

The applicable numeric targets for the Arivaca TMDL are the Arizona water quality standard of 0.2 µg/L mercury in the water column and the Arizona Fish Consumption Guideline criterion of 1 mg/kg mercury concentration in fish tissue. Arizona has adopted water quality standards for mercury that apply to a number of the designated uses specified for Arivaca Lake, including protection of aquatic life and wildlife and protection of human and agricultural uses. Of these numeric criteria, the most stringent is the chronic aquatic life criterion of 0.01 µg/L dissolved mercury (see table 7 on page 15 in the TMDL). Arizona has also issued a fish consumption advisory for this lake because mercury concentrations in fish tissue exceed 1 mg/kg.

Mercury bioaccumulates in the food chain. Within a lake fish community, top predators usually have higher mercury concentrations than forage fish, and tissue concentrations generally increase with age class. Top predators (such as largemouth bass) are often target species for sport fishermen. Arizona bases its Fish Consumption Guideline on average concentrations in a sample of sport fish. Therefore, the criterion should not apply to the extreme case of the most-contaminated age class of fish within a target species; instead, the criterion is most applicable to an average-age top predator. Within Arivaca Lake, the top predator sport fish is the largemouth bass. The selected target for the TMDL analysis is an average tissue concentration in 5-year-old largemouth bass of 1.0 mg/kg.

Source Assessment

A TMDL evaluation must examine all known potential sources of the pollutant in the watershed, including point sources, nonpoint sources, and background levels. The source assessment is used as the basis for developing a model and analyzing TMDL allocation options. There are no permitted point source discharges and no known sources of mercury-containing effluent in the Arivaca watershed. External sources of the mercury load to the lake include natural background load from the watershed, atmospheric deposition, and possible nonpoint load from past mining activities.

Watershed background load. The watershed background load of mercury was derived from mercury in the parent rock and from the net effects of atmospheric deposition of mercury on the watershed. Some mercury is also present within the parent rock formations of the Arivaca watershed, although no concentrated ore deposits are known.

The net contributions of atmospheric deposition and weathering of native rock were assessed by measuring concentrations in sediment of tributaries to Arivaca Lake. EPA collected 25 sediment and rock samples from dry tributaries in the Arivaca watershed and analyzed them for mercury. These data show that most of the sediment samples from the Arivaca watershed were considered at or near background mercury levels.

Nonpoint loadings from mining. No known mining for mercury itself has occurred in the watershed. However, mining activities for minerals other than mercury, especially historical mining practices for gold, might contribute to mercury loading in the watershed. Gold and silver mining commonly occurred in the area surrounding Arivaca Lake but apparently not within the watershed itself. The U.S. Bureau of Mines identified only one exploratory prospect, for manganese and uranium, within the Arivaca watershed.

Ruby Dump. Ruby Dump is in the southern portion of Arivaca watershed at the very upstream end of Cedar Canyon Wash. The dump apparently served the town of Ruby and the Montana Mine. The waste is characterized by numerous mining artifacts (e.g., crucibles) but also includes many common household items like bottles and plates. Samples were taken at three different locations of the Ruby Dump: the top of the hill (just below the fire pit), the middle of the hill, and the base of the dump. The mercury results for these samples, from the top of the hill to the bottom, were 1,467 ppb, 1,244 ppb (blind duplicate was 495 ppb), and 486 ppb. The average of these four samples is 918 ppb, which is the number used in the watershed modeling to represent the mercury concentration in sediment eroding from this site.

Near-field atmospheric deposition. Significant atmospheric point sources of mercury often cause locally elevated areas of near-field atmospheric deposition downwind. A review of *Mercury Study Report to Congress* (USEPA 1997c) and a search of EPA's AIRS database of permitted point sources found no significant U.S. sources of airborne mercury within or near the Arivaca watershed. Also, the most nearby parts of Mexico immediately to the southwest (prevailing wind direction) of the watershed are sparsely populated. Because of the lack of major nearby sources, especially sources along the axis of the prevailing wind, EPA does not believe that near-field atmospheric deposition of mercury attributable to individual emitters is a major component of mercury loading to the Arivaca watershed. Because no significant near-field sources of mercury deposition were identified, mercury from atmospheric deposition onto the watershed is treated as part of a general watershed background load in this analysis.

Far-field atmospheric deposition. In May 1997 the MDN began collecting deposition data at a new station in Caballo, in the southwestern quadrant of New Mexico. This station is the closest MDN station to the Arivaca Lake and was used to estimate loads to Arivaca Lake. Because the climate at Arivaca is wetter than that at Caballo, the distribution of wet and dry deposition is likely to be different. Monthly wet deposition rates at Arivaca were estimated as the product of the volume-weighted mean concentration for wet deposition at Caballo times the rainfall depth at Arivaca. This approach was used because volume-weighted mean concentrations are usually much more stable between sites than wet deposition rates, which are sensitive to rainfall amount. Dry deposition at Arivaca was then calculated as the difference between the total deposition rate at Caballo and the estimated Arivaca wet deposition rate. The estimates

derived for Arivaca were 5.3 μg/m^2/yr by wet deposition and 7.1 μg/m^2/yr by dry deposition. In sum, mercury deposition at Arivaca is assumed to be equivalent to that estimated for Caballo, New Mexico, but Arivaca is estimated to receive more wet deposition and less dry deposition than Caballo because more of the particulate mercury and reactive gaseous mercury that contribute to dry deposition are scavenged at a site with higher rainfall.

Loading Capacity—Linking Water Quality and Pollutant Sources

The linkage analysis in a TMDL defines the connection between numeric targets and identified sources. The linkage is defined as the cause-and-effect relationship between the selected indicators, the associated numeric targets, and the identified sources. This linkage analysis provides the basis for estimating total assimilative capacity and any needed load reductions. Specifically, for the linkage analysis in the Arivaca TMDL, models of watershed loading of mercury were used together with a model of mercury cycling and bioaccumulation in the lake. This approach enabled a translation between the numeric target (expressed as a fish tissue concentration of mercury) and mercury loading rates. The loading capacity was then determined through the linkage analysis as the mercury loading rate that is consistent with meeting the target fish tissue concentration.

Watershed model, Watershed-scale loading of water and sediment was simulated using the Generalized Watershed Loading Function (GWLF) model. The complexity of this loading function model falls between that of detailed simulation models (which attempt a mechanistic, time-dependent representation of pollutant load generation and transport) and simple export coefficient models (which do not represent temporal variability). GWLF provides a mechanistic, simplified simulation of precipitation-driven runoff and sediment delivery, yet it is intended to be applicable without calibration. Solids load, runoff, and ground water seepage can then be used to estimate particulate and dissolved-phase pollutant delivery to a stream, on the basis of pollutant concentrations in soil, runoff, and ground water. Applying the GWLF model to the period from October 1985 through September 1998 yielded an average of 11.0 cm/year runoff and 2,520,000 kg sediment yield by sheet and rill erosion. The sediment yield estimate is likely to be less than the actual yield rate from the watershed because mass wasting loads were not accounted for; however, mass wasting loads are thought to be of minor significance for loading of bioavailable mercury to the lake.

Estimates of watershed mercury loading were based on the sediment loading estimates generated by GWLF by applying a sediment potency factor. These estimates are shown in table D3. A background loading estimate was first calculated and then combined with estimates of loads from individual hot spots. Most of the EPA sediment samples showed no clear spatial patterns, with the exception of the hot spot area identified at Ruby Dump. Therefore, background loading was calculated using the central tendency of sediment concentrations from all samples excluding Ruby Dump. The background sediment mercury concentrations were assumed to be distributed lognormally, as is typical for environmental concentration samples, and an estimate of the arithmetic mean of 70.9 ppb was calculated from the observed geometric mean and coefficient of variation. Applying this assumption to the GWLF estimates of sediment transport yields an estimated rate of mercury loading from watershed background of 178.9 g/yr.

Table D3. Annual total mercury load to Arivaca Lake

Watershed year	Mercury loading to lake (g/year)			
	From watershed	From Ruby Dump	From direct atmospheric deposition to lake	Total
1986	170.16	0.65	4.208	175.018
1987	184.34	0.7	4.208	189.248
1988	205.61	0.79	4.208	210.608
1989	70.9	0.27	4.208	75.378
1990	198.52	0.76	4.208	203.488
1991	99.26	0.38	4.208	103.848
1992	163.07	0.62	4.208	167.898
1993	233.97	0.89	4.208	239.068
1994	141.8	0.54	4.208	146.548
1995	219.79	0.84	4.208	224.838
1996	170.16	0.65	4.208	175.018
1997	191.43	0.73	4.208	196.368
1998	276.51	1.06	4.208	281.778
Grand total	2,325.52	8.88	54.704	2,389.10
Annual average	178.89	0.68	4.21	183.78

Loading from the Ruby Dump was calculated separately, but it was also based on the GWLF estimate of sediment load generated per hectare of rangeland (the land use surrounding the hot spots), as reduced by the sediment delivery ratio for the watershed. The extent of the hot spot was observed to be 200 feet by 50 feet. The mercury concentration assigned to surface sediments at the dump was the arithmetic average of the four EPA samples taken in October 1997, or 918 ppb. From these assumptions, less than 1 percent of the watershed mercury load to Arivaca Lake appears to originate from Ruby Dump, which is the only identified hot spot in the watershed.

The direct deposition of mercury from the atmosphere onto the Arivaca Lake surface was calculated by multiplying the estimated atmospheric deposition rates times the lake surface area, resulting in a load of 4.2 g/yr.

Lake hydrology model. The water level in Arivaca Lake is not actively managed, and releases occur only when storage capacity is exceeded. Therefore, lake hydrology was represented by a simple monthly water balance. Applying the water balance model requires pan evaporation data as an input, in addition to the watershed meteorological data. Because no evaporation data were available at the local Cooperative Summary of the Day meteorological station, pan evaporation data for Tucson were used. Pan evaporation data for 1980 through 1995 were obtained from the BASINS 2.0 Region 9 data files. Later pan evaporation data were not available for Tucson, so monthly averages were used for the 1996 through 1998 water balance. The water balance model was run for the period 1985 through 1998. This water balance approach provides a rough approximation of the seasonal cycle of changes in volume and surface area of Arivaca

Lake and of the amount of water released downstream over the spillway. It cannot capture daily or event-scale movement of water in and out of the lake.

Mercury cycling and bioaccumulation model. Cycling and bioaccumulation of mercury within the lake were simulated using the D-MCM (EPRI 1999). D-MCM predicts the cycling and fate of the major forms of mercury in lakes, including methylmercury, Hg(II), and elemental mercury. D-MCM is a time-dependent mechanistic model, designed to consider the most important physical, chemical, and biological factors affecting fish mercury concentrations in lakes. It can be used to develop and test hypotheses, scope field studies, improve understanding of cause/effect relationships, predict responses to changes in loading, and help design and evaluate mitigation options.

Because strong anoxia in the hypolimnion is a prominent feature during summer stratification for the Arizona lakes simulated in this study, D-MCM was modified to explicitly allow significant methylation to occur in the hypolimnion. In previous applications of D-MCM, the occurrence of methylation was restricted to primarily within surficial sediments. That the locus of methylation likely includes or is even largely within the hypolimnion is supported by (1) the detection of very high methylmercury concentrations in the hypolimnia of Arivaca Lake and (2) almost complete losses of sulfate in Arivaca Lake in the hypolimnion resulting from sulfate reduction. An input was added to the model to specify the rate constant for hypolimnetic methylation, distinct from sediment methylation.

The results of the model calibration are shown in table D4. The model calculations are the predicted annual ranges after the model has reached steady state. The observed concentrations are from July 1997.

Table D4. Predicted and observed mercury for annual average load and flow

	Predicted	Observed
Methyl Hg: Water column (ng/L)	0.00–12.07	14.3
Hg II: Water column (ng/L)	0.00–6.28	1.46–8.3
Methyl Hg: 5-year-old largemouth bass (mg/kg)	1.18	1.18

Allocations

A TMDL represents the sum of all individual allocations of portions of the waterbody's loading capacity. Allocations may be made to point sources (wasteload allocations) or nonpoint sources (load allocations). The TMDL (sum of allocations) must be less than or equal to the loading capacity; it is equal to the loading capacity only if the entire loading capacity is allocated. In many cases, it is appropriate to hold a portion of the loading capacity in reserve to provide a margin of safety (MOS), as provided for in the TMDL regulation. The allocations and MOS are shown in table D5. These allocations, from the best currently available information, predict attainment of acceptable fish tissue concentrations within a time horizon of approximately 10 years. A delay in achieving standards is unavoidable because time will be required for mercury to cycle through the lake and food chain after load reductions occur.

Table D5. Summary of TMDL allocations and needed load reductions (in g-Hg/yr)

Source	Allocation	Existing load	Needed reduction
Wasteload allocations	0.0	0.0	0.0
Load allocations			
Atmospheric deposition	4.2	4.2	0
Ruby Dump	0.7	0.7	0
Watershed background	111.2	178.9	67.7
Total	116.1	183.8	67.7
Unallocated reserve	38.7		
Loading capacity	154.8		

The model was used to evaluate the load reductions necessary to meet the numeric target. The response of concentrations of mercury in 5-year-old largemouth bass to changes in external mercury loads is nearly linear. This is because the sediment burial rates are high and sediment recycling is low, with most of the methylmercury that enters the food chain being created in the anoxic portion of the water column. The model calculates that the numeric target of 1 mg/kg in 5-year-old largemouth bass is predicted to be met with a 16 percent reduction in total watershed loads to Arivaca Lake, which results in a loading capacity of 154.8 g/year of mercury.

There are uncertainties associated with mercury sources and the linkage between mercury sources and fish tissue concentrations in Arivaca Lake. As a result, the TMDL reserves 38.7 g-Hg/yr (25 percent of the loading capacity) for the MOS and allots the remaining load of 116.1 g-Hg/yr for sources. Because no permitted point source discharges occur within the Arivaca watershed, the wasteload allocation is zero and the load allocation is 116.1 g-Hg/yr.

The load allocation provides loads for three general sources: direct atmospheric deposition onto the lake surface, hot spot loading from Ruby Dump, and generalized background watershed loading, including mercury derived from parent rock and soil material, small amounts of residual mercury from past mining operations, and the net contribution of atmospheric deposition onto the watershed. Direct deposition to the lake surface is a small part of the total load and is believed to derive from long-range transport of global sources, which are not readily controllable. The load from Ruby Dump is also small. As a result, the TMDL does not require reductions from these sources, and their load allocations are their existing loads.

Background watershed loading appears to be the major source of mercury to Arivaca Lake. The intensive watershed survey conducted for this TMDL did not identify any significant terrestrial sources of mercury. Regarding air deposition to the watershed land surface, insufficient data were available to calculate reliable estimates of the proportion of mercury deposited from the air that actually reaches Arivaca Lake. Therefore, a load allocation of 111.2 g-Hg/yr was established for overall background watershed loading. This requires a 38 percent reduction from existing estimated loads from this source. This reduction is believed feasible for several reasons.

Potential for erosion control. Reduction of mercury loading from the watershed to Arivaca Lake depends on reduction in sediment erosion rates. Improved livestock management practices could obtain significant reductions in erosion rates. As a side benefit, implementation of livestock BMPs could result in significant reductions in loadings of DOC and nutrients to the lake. The availability of high levels of DOC and nutrients in the lake appears to affect the methylation process. Reduction of DOC and nutrient levels should reduce the efficiency of the methylation process at Arivaca Lake, effectively increasing the lake's mercury loading capacity.

Reductions in atmospheric deposition of mercury. Although no reliable estimates are available, new mercury air emissions to the environment appear to be declining. U.S. mercury emissions have declined significantly since 1990 and are expected to decline further upon implementation of new emission limits on incinerators as required by recent EPA regulations. Reductions in air deposition in Arivaca Lake watershed would eventually result in decreases in mercury loading to the lake itself.

Potential location and remediation of undiscovered mercury sources. Although investigation of the watershed did not reveal any significant localized sources of mercury in the watershed (with the possible exception of Ruby Dump), additional site investigation is warranted to ensure that no significant sources were missed. From past experience with mine site remediation in similar circumstances in Arizona, newly discovered sites could be effectively eliminated as ongoing mercury sources.

Alternative management strategies. Any alterations in rates of methylation or in rates of mercury loss to deep sediments will change the relationship between external mercury load and fish tissue concentration and would thus result in a change in the loading capacity for external mercury loads. The loading capacity could be increased by management intervention methods that decrease rates of bacterial methylmercury production within the lake or increase rates of burial and sequestration of mercury in lake sediment. Selection of such an approach would require further research and feasibility studies. Some alternative strategies that might be suitable for further investigation include the following:

- Hypolimnion aeration or mixing
- Sulfur chemistry modification
- Alum treatment
- Reduction of DOC and nutrient levels
- Dredging of lake sediments

III. McPhee and Narraguinnep Reservoirs, Colorado

Description of the Applicable Water Quality Standards

The TMDL for McPhee and Narraguinnep Reservoirs in southwestern Colorado was based on the Fish Consumption Advisory action level of 0.5 mg/kg mercury concentration in fish tissue. Colorado Department of Public Health and the Environment listings are based on the risk analysis presented in the May 6, 1991, Disease Control and

Epidemiology Division position paper for *Draft Colorado Health Advisory for Consumption of Fish Contaminated with Methylmercury.* This paper, using a toxicity value RfD of 0.3 µg/kg/day, establishes a fish tissue concentration of 0.5 mg/kg as the approximate center of the range at which the safe consumption level is four meals per month for nonpregnant adults and one meal per month for women who are pregnant, nursing, or planning to become pregnant and children nine years of age or younger. The criterion is applied to an average-age top predator. In McPhee Reservoir, the top predator among sport fish regularly taken is the smallmouth bass (19 percent of the total catch in 1993); the top predator sport fish in Narraguinnep Reservoir is the walleye. The lake water quality model D-MCM (EPRI 1999) is capable of predicting mercury concentrations in fish tissue for each age class at each trophic level. Average mercury concentrations in fish tissue of target species are assumed to be approximated by the average concentration in 15-inch smallmouth bass in McPhee and the 18-inch walleye in Narraguinnep. Therefore, the selected target for the TMDL analysis in McPhee Reservoir is an average tissue concentration in 15-inch smallmouth bass of 0.5 mg/kg or less. The selected target in Narraguinnep Reservoir is the 18-inch walleye of 0.5 mg/kg or less.

Source Assessment

McPhee and Narraguinnep reservoirs have several sources of mercury. The sources external to the reservoirs separate into direct atmospheric deposition onto the lakes (from both near- and far-field sources) and transport into the lakes from the watershed. The watershed loading occurs in both dissolved and sediment-sorbed forms. Ultimate sources in the watershed include mercury in parent rock, mercury residue from mine tailings and mine seeps, point source discharges, and atmospheric deposition onto the watershed, including deposition and storage in snowpack. A summary of the mercury load estimates for McPhee Reservoir is presented in table D6.

Table D6. Summary of mercury load estimates for McPhee Reservoir

Reservoir	Water-shed runoff (g/yr)	Water-shed sediment (g/yr)	Inter-basin transfer (g/yr)	Atmos. deposition (g/yr)	Total (g/yr)	Load per volume (mg/ac-ft)	Load per surface area (mg/m^2)
McPhee	2,576	222		251	3,049	4.66	0.098
Narraguinnep	2.7	22.7	15.9	36.8	78.1	4.59	0.035

Past mining activities likely provide an important source of mercury load to the McPhee and Narraguinnep watershed. There are large mining districts in the Dolores River watershed, the LaPlata, the Rico, and the area around Dunton on the West Dolores River. The quantity of mercury loading from mining operations has been estimated through a combination of observed data in the water column and sediment coupled with the watershed linkage analysis.

Significant atmospheric point sources of mercury often cause locally elevated areas of near-field atmospheric deposition downwind. Two large coal-fired power plants are in the Four Corners area within about 50 miles of the McPhee and Narraguinnep reservoirs. The plants in the Four Corners area (2,040 megawatt (MW) capacity) and the Navajo plant (1,500 MW capacity) are upwind of McPhee and Narraguinnep reservoirs. It is likely that the

mercury emitted from these plants contributes to the mercury loading of the two reservoirs. Because no direct measurements of atmospheric deposition of mercury are available, EPA cannot assess the significance of this loading and must await further investigation, including the establishment of a mercury deposition monitoring site in the area.

Loading Capacity—Linking Water Quality and Pollutant Sources

Models of watershed loading of mercury are combined with a model of mercury cycling and bioaccumulation in the lake to translate the numeric target, expressed as a fish tissue concentration of mercury, to mercury loading rates. The coupled models estimate mercury loading to the reservoirs and predict mercury cycling and speciation within the reservoir. An estimated load reduction of 52 percent is needed for long-term average mercury concentrations in a standardized 15-inch smallmouth bass to drop to 0.5 mg/kg wet muscle.

Allocations

The loading capacity for McPhee Reservoir was estimated to be 2,592 g/year of mercury. Narraguinnep Reservoir's loading capacity was estimated at 39.1 g/year of mercury. This is the maximum rate of loading consistent with meeting the numeric target of 0.5 mg/kg in fish tissue. Because of the uncertainties regarding the linkage between mercury sources and fish tissue concentrations in McPhee and Narraguinnep reservoirs, an allocation of 70 percent of the loading capacity was used for this TMDL. The TMDL calculated for McPhee Reservoir is equivalent to a total annual mercury loading rate of 1,814 g/yr (70 percent of the loading capacity of 2,592 g/yr), while that for Narraguinnep Reservoir is equivalent to a total annual mercury loading rate of 27.3 g-Hg/yr (70 percent of 39.1 g-Hg/yr). Summaries of the TMDL allocations and needed load reductions for the McPhee and Narraguinnep Reservoirs are presented in tables D7 and D8, respectively.

Table D7. Summary of TMDL allocations and needed load reductions for McPhee Reservoir

Source	Allocation	Existing load	Needed reduction
Atmospheric deposition	63	251	188
Rico/Silver Creek mining area	507	1030	523
Dunton mining area	348	708	360
La Plata mining area	69	141	72
Watershed background	827	919	92
Total	1,814	3,049	1,235
Unallocated reserve	778		
Loading capacity	2,592		

Note: Measurements in g/year of mercury.

Table D8. Summary of TMDL allocations and needed load reductions for Narraguinnep Reservoir

Source	Allocation	Existing load	Needed reduction
Atmospheric deposition	9.2	36.8	27.6
Interbasin transfer from McPhee Reservoir	9.5	15.9	6.4
Watershed background	8.6	25.4	16.8
Total	27.3	78.1	50.8
Unallocated reserve	11.8		
Loading capacity	39.1		

Note: Measurements in g/year of mercury.

IV. Clear Lake, California

Description of the Applicable Water Quality Standards

EPA promulgated the California Toxics Rule (CTR) in May 2000 (65 FR 31682). The CTR contains a water quality criterion of 50 ng/L total recoverable mercury for water and organism consumption and is intended to protect humans from exposure to mercury in drinking water and through fish and shellfish consumption. This criterion is enforceable in California for all waters with a municipal or domestic water supply designated use and is applicable to Clear Lake. However, the state of California does not consider this criterion sufficiently protective of the consumers of fish from Clear Lake.

The water quality management plan or Basin Plan for the Central Valley Regional Water Quality Control Board adopted new water quality standards for mercury for Clear Lake at the same time it adopted mercury TMDLs for Clear Lake. The state's water quality criteria are for fish tissue and are intended to protect designated uses for fishing and wildlife habitat. The applicable criteria are 0.09 mg/kg and 0.19 mg/kg of mercury in fish tissue for trophic levels 3 and 4 fish, respectively. These levels were recommended by the U.S. Fish and Wildlife Service to protect wildlife, including osprey and bald eagles, at Clear Lake; these levels allow adults to safely consume about 3.5 fish meals per month (26 grams/day) if eating mainly trophic level 4 fish such as catfish and bass. The 26 grams/day assumes a diet composed of 70 percent trophic level 4 fish and 30 percent trophic level 3 fish. The 90th percentile consumption rate of a small group of residents of Clear Lake, primarily members of the Elem Pomo Indian Tribe, is 30 grams/day of Clear Lake fish, as reported in 1997.

Source Assessment

Clear Lake is in Lake County in northern California. It is a shallow, eutrophic waterbody that consists of three basins—the Upper, Lower, and Oaks Arms. It is the largest natural lake entirely within California's boundaries. Tourism and sport fishing are important sectors of the local economy. Five American Indian tribes use the resources of the lake and its watershed.

The Clear Lake watershed lies within a region naturally enriched in mercury. The Sulphur Bank Mercury Mine (SBMM) site, on the shores of Oak Arm, was a highly productive source of mercury between 1872 and 1957. Similar smaller mines were

present in the Clear Lake watershed, all of which are now inactive. Levels of mercury in Clear Lake sediments rose significantly after 1927, when open-pit operations became the dominant mining method at SBMM. EPA declared the SBMM a federal Superfund site in 1991, and since then several remediation projects have been completed, including regrading and vegetation of mine waste piles along the shoreline and construction of a diversion system for surface water runoff. EPA is conducting a remedial investigation to fully characterize the SBMM site to propose final remedies.

Inorganic mercury loads entering Clear Lake come from ground water and surface water from the SBMM site; tributaries and other surface water that flows directly into the lake; and atmospheric deposition, including atmospheric flux from SBMM. Some mercury deposited historically in the lake due to mining operations or erosion at SBMM might also contribute to mercury concentrations in fish today.

Ground water and surface water from the SBMM site. SBMM covers approximately 1 square mile on the east shore of the Oaks Arm of Clear Lake. The site contains approximately 120 acres of exposed mine overburden and tailings (referred to as waste rock). Two small unprocessed ore piles are also on the site. Mercury in samples of mine materials ranged from 50 to 4,000 mg/kg. All piles of mine materials exhibit the potential to generate acid rock drainage. The abandoned mine pit, the Herman Impoundment, is filled with 90 feet of acidic water (pH 3) and has a surface area of about 20 acres. The average concentrations in the Herman Impoundment of water and sediment are around 800 ng/L and 26 mg/kg, respectively. A geothermal vent at the bottom of the impoundment continues to discharge gases, minerals (including mercury), and fluids into the pit.

A large pile of waste rock, known as the waste rock dam (WRD), stretches about 2,000 feet along the shore of the western side of the SBMM site. The WRD lies between Herman Impoundment and Clear Lake. The surface water in the impoundment is 10–14 feet above the surface of Clear Lake, which creates a gradient of ground water flow toward the lake. Surface runoff from the northern side of the site is bounded by a wetland that drains to Clear Lake. Surface runoff from the northern waste rock piles is directed through culverts into the northern wetland. In 1990 rock and geofabric barriers were installed at the culverts to reduce the transport of suspended solids. The northern wetland is used for cattle grazing and as a source of fish, tules, and other resources used by the members of the Elem Pomo Tribe. Waste rock piles extend into the wetlands.

Inputs of mercury from SBMM are estimated to be between 1 and 568 kg/year. EPA Superfund program's estimate of mercury transported in ground water from the WRD is used as the lower-bound input. Regional Board staff estimate that 568 kg/year is the maximum upper-bound estimate of all inputs from SBMM, including past and continuing contributions to the active sediment layer. This is approximately 96.5 percent of total sources.

Ground water from SBMM appears to contribute mercury that is readily methylated, relative to mercury from other inputs. Ground water flow from the mine site has been detected entering Clear Lake by subsurface flow through lake sediments. Mercury in ground water from the WRD is solubilized and likely in chemical forms that are easily taken up by methylating bacteria. Acidic drainage from the mine site also contains high

sulfate concentrations that enhance the rates of methylation by sulfate-reducing bacteria. This assertion is supported by data showing that methylation rates near the mine site are significantly higher than those in other parts of Clear Lake. In contrast to the mercury in SBMM ground water, the mercury in lakebed and tributary sediments originates primarily as cinnabar, which has low solubility in water.

Tributaries and other surface water flowing directly into the lake. Mercury entering Clear Lake from its tributaries originates in runoff from naturally mercury-enriched soils, sites of historical mining activities, and mercury deposited in the watershed from the atmosphere. Geothermal springs might contribute to tributary loads, especially in the Schindler Creek tributary to Oaks Arm. Tributary and watershed runoff loads of mercury range from 1 to 60 kg/year, depending on flow rates. Loads in average water years are 18 kg/year, approximately 3 percent of the total sources.

Geothermal springs and lava tubes that directly discharge to Clear Lake do not appear to be significant sources of mercury. Mercury concentrations in surficial sediment samples collected near lakebed geothermal springs were not elevated relative to levels in sediment away from geothermal springs.

Atmospheric deposition, including flux from the SBMM site. Small amounts of mercury deposit directly on the surface of Clear Lake from the global atmospheric pool and potentially from local, mercury-enriched sources. Atmospheric loads to the lake surface from the global pool were estimated using data from MDN monitoring stations in Mendocino County and San Jose. Estimates ranged from 0.6 to 2.0 kg/year, approximately 0.3 percent of the total sources.

Loading Capacity––Linking Water Quality and Pollutant Sources

The Regional Board staff assumes that there is a directly proportional relationship between methylmercury in fish and mercury in the surficial sediment. This is a simplification of a highly complex process. Many factors, such as sulfide and sulfate concentrations, temperature, and organic carbon, affect methylation or concentrations of methylmercury. Factors that affect accumulation of methylmercury in fish include species, growth rate, prey availability, and the like. To reduce levels of methylmercury in fish, loads of mercury to the lake must be reduced. Section 5.3.1 of the Staff Report provides examples of remediation projects demonstrating that removal of inorganic mercury from a range of aquatic environments has been effective in reducing concentrations of mercury in fish.

A set of first-order relationships, each controlled by a single variable of concentration of mercury or methylmercury, provide the basis for the assumption of a directly proportional relationship between mercury in fish and in surficial sediment in Clear Lake. Concentrations of methylmercury in water and methylmercury in biota are related by BAFs. Relationships between methylmercury in the water column and in sediment can be described as a flux rate of methylmercury from sediment. Concentrations of methylmercury and mercury in sediment are related through calculation of a methylation efficiency index (ratio of methylmercury to mercury in surficial sediment).

In each of these steps in the linkage analysis, one variable is related to another by a simple ratio or linear equation. For example, BAFs are calculated by dividing the

concentration of methylmercury in fish by the concentration of methylmercury in the water. Data are available to determine BAF and methylation indices that are specific for Clear Lake. With the current understanding of the transport, methylation, and uptake processes in Clear Lake, the Regional Board staff was unable to refine these relationships to incorporate the effects of other factors. The end result was that methylmercury in biota was related linearly to mercury in surficial sediment.

Meeting the recommended water quality standards would require reducing existing fish tissue concentrations by 60 percent. Using the linear relationship, the linkage analysis indicates that overall mercury loads to Clear Lake sediment must be reduced by 60 percent to reduce methylmercury concentrations in fish tissue by the proportional amount. The Regional Board is establishing the assimilative capacity of inorganic mercury in Clear Lake sediments as 70 percent of existing levels to include a margin of safety of 10 percent to account for the uncertainties in the linkage analysis.

Allocations

The strategy for meeting the fish tissue criteria is to reduce the inputs of mercury to the lake from tributaries and the SBMM site, combined with active and passive remediation of contaminated lake sediments. The load allocations for Clear Lake will result in a reduction in the overall mercury sediment concentration by 70 percent of existing concentrations. The load allocations are assigned to the active sediment layer of the lakebed, the SBMM terrestrial site, the tributary creeks and surface water runoff to Clear Lake, and atmospheric deposition. Table D9 summarizes the load allocations. The load allocation to the active sediment layer is expressed as reducing concentrations of mercury in the active sediment layer to 30 percent of current concentrations. The load allocation to the SBMM terrestrial site is 5 percent of the ongoing loads from the terrestrial mine site. The load allocation for the mine also includes reducing mercury concentrations in surficial sediment to achieve the sediment compliance goals for Oaks Arm, shown in table D10. The load allocation to tributary and surface water runoff is 80 percent of existing loads. These load allocations account for seasonal variation in mercury loads, which vary with water flow and rainfall. The analysis includes an implicit margin of safety in the reference doses for methylmercury that were used to develop the fish tissue objectives. It also includes an explicit margin of safety of 10 percent to account for uncertainty in the relationship between fish tissue concentrations and loads of mercury. The reductions in loads of mercury from all sources are expected to result in attainment of water quality objectives.

Table D9. Summary of mercury load allocations

Source	Existing load (kg/year)	Needed reduction
Clear Lake sediment	695	70% of existing concentration
Sulphur Bank Mercury Mine		95% of existing load
Tributaries	18	20% of existing load
Atmosphere	2	no change

Table D10. Sediment goals for mercury in Clear Lake

Site designation	Location	Sediment mercury goal (mg/kg dry weight)[a]
Upper Arm UA-03	Center of Upper Arm on transect from Lakeport to Lucerne	0.8
Lower Arm LA-03	Center of Lower Arm, north and west of Monitor Point	1.0
Oaks Arm		
OA-01[b]	0.3 km from SBMM 0.3 km from SBMM	16[c]
OA-02[b]	0.8 km from SBMM	16[c]
OA-03[b]	1.8 km from SBMM	16
OA-04[b]	3.0 km from SBMM	10
Narrows O1	7.7 km from SBMM	3

Notes:

[a]Sediment goals are 30 percent of existing concentrations. Existing concentrations are taken as the average mercury concentrations in samples collected in 1996–2000 (Clear Lake Basin Plan Amendment Staff Report).

[b]Sediment goal is part of the load allocation for SBMM.

[c]Due to the exceptionally high concentrations existing at the eastern end of Oaks Arm, sediment goals at OA-01 and OA-02 are not 70 percent of existing concentrations. These goals are equal to the sediment goal established for OA-03.

Clear Lake sediment. Reducing mercury concentrations in surficial sediment by 70 percent is an overall goal for the entire lake. To achieve water quality objectives, extremely high levels of mercury in the eastern end of Oaks Arm near SBMM must be reduced by more than 70 percent. To evaluate progress in lowering sediment concentrations, the following sediment compliance goals are established at sites that have been sampled previously.

Sulphur Bank Mercury Mine. Current and past releases from SBMM are a significant source of mercury loading to Clear Lake. Ongoing annual loads from the terrestrial mine site to the lakebed sediments occur through ground water, surface water, and atmospheric routes. Loads from ongoing releases from the terrestrial mine site should be reduced to 5 percent of existing inputs. Because of its high potential for methylation relative to mercury in lakebed sediments, mercury entering the lake through ground water from the mine site should be reduced to 0.5 kg/year.

Past releases from the mine site are a current source of exposure through remobilization of mercury that exists in the lakebed sediments as a result of past releases to the lake from the terrestrial mine site. Past active mining operations, erosion, and other mercury transport processes at SBMM have contaminated sediment in Oaks Arm. The load allocation assigned to SBMM includes reducing surficial sediment concentrations in Oaks Arm by 70 percent (more at sites nearest the mine site) to meet the sediment compliance goals in table D10.

EPA anticipates implementing additional actions to address the ongoing surface and ground water releases from SBMM over the next several years. These actions are expected to lead to significant reductions in the ongoing releases from the mine pit, the mine waste piles, and other ongoing sources of mercury releases from the terrestrial mine

site. EPA also plans to investigate what steps are appropriate under the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) to address the existing contamination in the lakebed sediments from past releases from SBMM. The Regional Board will continue to work closely with EPA on these important activities. In addition, the Regional Board will coordinate monitoring activities to investigate other sources of mercury loads to Clear Lake. These investigations by EPA and the Regional Board should reduce the uncertainty that exists regarding the annual load of mercury to the lake, the contribution of each source to that load, and the degree to which those sources lead to methylmercury exposure of and mercury uptake by fish in the lake. This information should lead to more refined decisions about what additional steps are appropriate and feasible to achieve the applicable water quality criteria.

Tributaries and surface water runoff. Past and current loads of mercury from the tributaries and direct surface water runoff are also a source of mercury loading to the lake and to the active sediment layer in the lakebed. This section excludes loads from surface water runoff associated with SBMM, which are addressed separately above. The loads of mercury from the tributaries and surface water runoff to Clear Lake should be reduced by 20 percent of existing levels. In an average water year, existing loads are estimated to be 18 kg/year. Loads range from 1 to 60 kg/year, depending on water flow rates and other factors. The load allocation applies to tributary inputs as a whole, instead of to individual tributaries. Efforts should be focused on identifying and controlling inputs from hot spots. The U.S. Bureau of Land Management, U.S. Forest Service, other land management agencies in the Clear Lake Basin, and Lake County will submit plans for monitoring and implementation to achieve the necessary load reductions. The Regional Board will coordinate with those agencies and other interested parties to develop the monitoring and implementation plans. The purpose of the monitoring is to refine load estimates and identify potential hot spots of mercury loading from tributaries or direct surface runoff into Clear Lake. Hot spots can include erosion of soils with concentrations of mercury above the average for the rest of the tributary. If significant sources are identified, the Regional Board will coordinate with the agencies to develop and implement load reductions. The implementation plans will include a summation of existing erosion control efforts and a discussion of feasibility and proposed actions to control loads from identified hot spots. The agencies will provide monitoring and implementation plans within five years after the effective date of this amendment and implement load reduction plans within five years thereafter. The goal is to complete the load reductions within 10 years of implementation plan approval.

The Regional Board will work with the American Indian tribes in the Clear Lake watershed on mercury reduction programs for the tributaries and surface water runoff. It will solicit the tribes' participation in developing monitoring and implementation plans.

Wetlands. The Regional Board is concerned about the potential for wetland areas to be significant sources of methylmercury. Loads and fate of methylmercury from wetlands that drain to Clear Lake are not fully understood. The potential for production of methylmercury should be assessed during the planning of any wetlands or floodplain restoration projects within the Clear Lake watershed. The Regional Board established a goal of no significant increases of methylmercury to Clear Lake resulting from such activities. As factors contributing to mercury methylation are better understood, the

Regional Board should examine the possible control of existing methylmercury production within tributary watersheds.

Atmospheric deposition. Atmospheric loads of mercury originating outside the Clear Lake watershed and depositing locally are minimal. Global and regional atmospheric inputs of mercury are not under the jurisdiction of the Regional Water Board. Loads of mercury from outside the Clear Lake watershed and depositing from air onto the lake surface are established at the existing input rate, estimated to be 1 to 2 kg/year.

V. Cache Creek, California

Description of the Applicable Water Quality Standards

EPA promulgated the California Toxics Rule (CTR) in May 2000 (65 FR 31682). The CTR contains a water quality criterion of 50 ng/L total recoverable mercury for waters designated for water and organism consumption, and it was intended to protect humans from exposure to mercury in drinking water and through fish and shellfish consumption. This criterion is enforceable in California for all waters with a municipal or domestic water supply designated use, and it is applicable to all waters in the Cache Creek watershed. The State of California, however, does not consider this criterion sufficiently protective of human and wildlife consumers of fish in the watershed.

The water quality management plan or Basin Plan for the Central Valley Regional Water Quality Control Board adopted new water quality standards for mercury for Cache Creek, Bear Creek, and Harley Gulch at the same time it adopted mercury TMDLs for those waterbodies. The state's water quality criteria are expressed as concentrations in fish tissue and are intended to protect designated uses, which include human and wildlife fish consumption. The applicable criteria are as follows: for Cache Creek and Bear Creek, the average methylmercury concentration shall not exceed 0.23 mg methylmercury/kg wet weight of muscle tissue in trophic level 4 fish 250–350 mm (piscivorous species, including bass and catfish), and 0.12 mg methylmercury/kg wet weight of muscle tissue in trophic level 3 fish 250–350 mm, or if not available, a minimum of 125 mm (bluegill, sunfish, and sucker); for Harley Gulch, the average methylmercury concentration shall not exceed 0.05 mg methylmercury/kg wet weight in whole, trophic level 2 and 3 fish 75–100 mm total length (hardhead, California roach, or other small resident species). Because Harley Gulch does not support larger, trophic level 3 and 4 fish, no water quality criteria for these larger fish were proposed in that waterbody.

These water quality standards permit safe consumption of about 22–40 g/day of Cache or Bear Creek fish (3 to 5.4 meals/month). In Cache and Bear creeks, the standards protect wildlife species, including bald eagle, peregrine falcon (state endangered), river otter, American mink, mergansers, grebes, and kingfishers. In Harley Gulch, the standards protect wildlife species, including small mammals, herons, and kingfishers.

Source Assessment

The Cache Creek watershed is impaired due to elevated levels of mercury in the water and in fish tissue. Because Cache Creek is a primary source of mercury to the Sacramento-San Joaquin Delta Estuary, lowering mercury levels in the Cache Creek watershed will assist in protecting human and wildlife health in the delta. The TMDL

encompasses the 81-mile reach of Cache Creek between Clear Lake Dam and the outflow of the Cache Creek Settling Basin, Bear Creek from its headwaters to its confluence with Cache Creek, and the 8-mile length of Harley Gulch.

Sources of mercury entering the watershed include waste rock and tailings from historical mercury mines, erosion of naturally mercury-enriched soils, geothermal springs, and atmospheric deposition. There are multiple inactive mercury mines in the Cache Creek watershed. The Sulphur Bank Mercury Mine contributes mercury to Cache Creek at the Clear Lake outflow. The Sulphur Creek mining district includes eight mines that drain predominately to Bear Creek via Sulphur Creek and four mines in the Bear Creek Basin. Harley Gulch receives inputs from the Turkey Run and Abbott mines. The Reed Mine drains to Davis Creek, a tributary to Cache Creek.

Historical mining activities in the Cache Creek watershed discharged and continue to discharge large volumes of inorganic mercury (termed total mercury) to creeks in the watershed. Much of the mercury discharged from the mines is now distributed in the creek channels and floodplain downstream from the mines. Natural erosion processes can be expected to slowly move the mercury downstream out of the watershed over the next several hundred years. However, current and proposed activities in and around the creek channel can enhance mobilization of this mercury. Activities in upland areas, such as road maintenance and grazing and timber activities, can add to the mercury loads reaching Cache Creek, particularly when the activities take place in areas that have elevated mercury levels. Mercury can be transformed to methylmercury in sediment by sulfate-reducing bacteria.

Cache Creek. In Cache Creek the watershed above Rumsey is the major source of methylmercury. The highest concentrations and production rates were observed below the mercury mines in Harley Gulch, in Sulphur and Bear creeks, and in the canyon above Rumsey. Lower methylmercury concentrations in water were measured in the North Fork and Cache Creek below Clear Lake Dam, which have lower inorganic mercury concentrations in sediment.

The sources of total mercury in Cache Creek largely parallel the sources of methylmercury. Most mercury derives from the watershed upstream of Rumsey. On a five-year average, mercury loads from the mine-related tributaries (Bear Creek, Harley Gulch, and Davis Creek), North Fork Cache Creek and Clear Lake contributed about 15 percent of the mercury loads measured in Cache Creek at Rumsey. In years with high degrees of runoff or extreme erosional events, inputs from the inactive mines would be much greater. The majority of the inorganic mercury loads were from unnamed sources, which include smaller, unmeasured tributaries and mercury in the Cache Creek bed and banks. Clean sediment entering the watershed below Rumsey diluted sediment mercury concentrations.

Bear Creek. The Bear Creek watershed upstream of all mine inputs contributes less than 10 percent to each of the loads of methylmercury and total mercury in Bear Creek. Sulphur Creek contributes about half of each of the methylmercury and total mercury loads in Bear Creek. The remainder of the Bear Creek methylmercury likely comes from production within the channel and seepage of underground springs. The rest of the mercury load in Bear Creek likely derives from the remobilization of mine waste deposited in the floodplain.

Harley Gulch. Much of the methylmercury in Harley Gulch is likely produced in a wetland area in the West Branch Harley Gulch, downstream of the inactive mercury mines. Over 90 percent the total mercury load in Harley Gulch is estimated to come from the West Branch, where the mines are. Total mercury loads from the mines may be underestimated due to a lack of data collected during heavy rainfall events. An alluvial fan, likely containing mine waste, at the confluence of Harley Gulch and Cache Creek, might contribute to the unknown source of mercury in the Cache Creek canyon.

Loading Capacity––Linking Water Quality Pollutant Sources

Total mercury in the creeks is converted to methylmercury by bacteria in the sediment. The concentration of methylmercury in fish tissue is directly related to the concentration of methylmercury in the water. The concentration of methylmercury in the water column is controlled in part by the concentration of total mercury in the sediment and the rate at which the total mercury is converted to methylmercury. The rate at which total mercury is converted to methylmercury varies from site to site; some sites (wetlands and marshes) having greatly enhanced methylation rates.

The linkage analysis describes the relationship between methylmercury concentrations in water and in large fish. Data collected in 2000 and 2001 show statistically significant relationships between concentrations of aqueous unfiltered methylmercury in water and large trophic level 3 and 4 fish. In Cache Creek, large trophic level 3 fish tissue concentrations (Sacramento sucker), normalized to 290 mm (from Slotten et al. 2004), were regressed against aqueous unfiltered methylmercury concentrations ($Y= 584.8X + 30.2$; $P < 0.001$, $R2 = 0.98$). In Cache Creek, large trophic level 4 fish tissue concentrations (largemouth bass, small mouth bass, and pikeminnow, depending on site), normalized to 305 mm (from Slotton et al. 2004), were regressed against aqueous unfiltered methylmercury concentrations ($Y = 2970.8X – 180.6$; $P < 0.01$, $R2 = 0.9$). Using these relationships, staff determined concentrations of unfiltered methylmercury in water that correspond to the proposed criteria for trophic levels 3 and 4 fish (0.12 mg/kg and 0.23 mg/kg, respectively). These concentrations are 0.15 ng/l for trophic level 3 fish and 0.14 ng/L for trophic level 4 fish. To ensure meeting both fish tissue criteria, staff selected 0.14 ng/L as the aqueous unfiltered methylmercury goal for Cache Creek.

For Bear Creek, the methylmercury goal of 0.06 ng/L represents the best estimate of the annual, median aqueous (unfiltered) concentration of methylmercury needed to attain the target of 0.23 mg/kg wet weight in trophic level 4 fish. Harley Gulch has no trophic level 4 fish, so the above relationships could not be used. Based on bioaccumulation factors specific to Harley Gulch, the aqueous methylmercury goal for Harley Gulch is 0.09 ng/L.

Allocations

The TMDL presents a plan to reduce mercury and methylmercury loads. Reducing the methylmercury loads will require a multi-faceted approach that includes controlling inorganic mercury loads and limiting the entry of inorganic mercury into sites with high rates of methylmercury production. Inorganic mercury loads may be controlled through remediation of mercury mines, erosion control, removal of highly contaminated sediment, and other activities. In addition to addressing inorganic mercury loads, the TMDL discusses limits to the production of methylmercury in constructed

impoundments, such as gravel pits and water storage facilities. Identification and evaluation of the unknown mercury source(s) in the upper basin are essential to attain the Cache Creek methylmercury targets in fish tissue and to help reduce mercury in sediment of the Sacramento-San Joaquin Delta Estuary.

Since methylmercury in the water column is directly related to mercury levels in fish, the following methylmercury load allocations are assigned to tributaries and the main stem of Cache Creek.

Methylmercury Load Allocations. Tables D11 and D12 provide methylmercury load allocations for Cache Creek, its tributaries, and instream methylmercury production. Allocations are expressed as a percent of existing methylmercury loads. The methylmercury allocations will be achieved by reducing the annual average methylmercury (unfiltered) concentrations to site- specific, aqueous methylmercury goals, which are 0.14 ng/L in Cache Creek, 0.06 ng/L in Bear Creek, and 0.09 ng/L in Harley Gulch. The allocations in tables D11 and D12 apply to sources of methylmercury entering each tributary or stream segment. In aggregate, the sources to each tributary or stream segment must have reductions of methylmercury loads as shown below.

Table D12 provides the load allocation within Bear Creek and its tributaries to attain the allocation for Bear Creek described in table D11. The inactive mines listed in the implementation summary are assigned a 95 percent total mercury load reduction. These mines include mines in the Harley Gulch Sulphur Creek and Bear Creek watersheds. Reductions in mercury loads from mines, erosion, and other sources in the Sulphur Creek watershed are expected to reduce in-channel production of methylmercury to meet the Sulphur Creek methylmercury allocation.

Table D11. Cache Creek methylmercury allocations

Source	Existing annual load (g/yr)	Acceptable annual load (g/yr)	Allocation (% of existing load)
Cache Creek (Clear Lake to North Fork confluence)	36.8	11	30%
North Fork Cache Creek	12.4	12.4	100%
Harley Gulch	1.0	0.04	4%
Davis Creek	1.3	0.7	50%
Bear Creek at Highway 20	21.1	3	15%
Within-channel production and ungauged tributaries	49.5	32	65%
		7[a]	10%[a]
Total of loads	122	66	54%
Cache Creek at Yolo[b]	72.5	39	54%
Cache Creek Settling Basin Outflow[c]	87	12	14%

Notes:

[a]The allocation includes a margin of safety, which is set to 10% of the acceptable loads. In terms of acceptable annual load estimates, the margin of safety is 7 g/yr.

[b]Cache Creek at Yolo is the compliance point for the tributaries and Cache Creek channel for meeting the allocations and aqueous goals. Agricultural water diversions upstream of Yolo remove methylmercury (50 g/yr existing load).

[c]The Settling Basin Outflow is the compliance point for methylmercury produced in the Settling Basin.

Table D12. Bear Creek methylmercury allocations

Source	Existing Annual Load (g/yr)	Acceptable Annual Load (g/yr)	Allocation (% of existing load)
Bear Creek at Bear Valley Road	1.7	0.9	50%
Sulphur Creek	8	0.8	10%
In-channel production and ungauged tributaries	11.4	1	10%
		0.3[a]	10%[a]
Total of loads	21.1	3	15%
Bear Creek at Highway 20[b]	21.1	3	15%

Notes:

[a]The allocation includes a margin of safety, which is set to 10% of the acceptable loads. In terms of acceptable annual load estimates, the margin of safety is 0.3 g/yr.

[b]Bear Creek at Highway 20 is the compliance point for Bear Creek and its tributaries.

To achieve the water quality objectives and the methylmercury allocations listed in tables D11 and D12, the following actions are needed: (1) reduce loads of total mercury from inactive mines; (2) where feasible, implement projects to reduce total mercury inputs from existing mercury-containing sediment deposits in creek channels and creek banks downstream from historical mine discharges; (3) reduce erosion of soils with enriched total mercury concentrations; (4) limit activities in the watershed that will increase methylmercury discharges to the creeks and, where feasible, reduce discharges of methylmercury from existing sources; and (5) evaluate other remediation actions that are not directly linked to activities of a discharger. Because methylmercury is a function of total mercury, reductions in total mercury loads are needed to achieve the methylmercury load allocations. Methylmercury allocations will be achieved in part by natural erosion processes that remove mercury that has deposited in creek beds and banks since the start of mining.

The proposed Basin Plan Amendment for mercury in San Francisco Bay assigns a reduction in total mercury loads from the Sacramento–San Joaquin River Delta of 110 kg/yr. Cache Creek is a major source of mercury to the Delta. To attain the San Francisco Bay reduction, loads of total mercury exiting Cache Creek should be reduced. Reductions in total mercury loads to the inactive mines in Harley Gulch and the Bear Creek watershed assigned by this TMDL and proposed changes to the Cache Creek Settling Basin, which would increase the mass of mercury retained in the basin, would create significant reductions in loads from Cache Creek.

VI. Minnesota Statewide[27] Mercury Total Maximum Daily Load

Description of the Applicable Water Quality Standards and TMDL Target

Minnesota Rules Chapters 7050.0222 and 7052.0100 set forth chronic numeric water quality standards based on total mercury concentrations in the water column. The wildlife-based standard applicable to only the waters of the Lake Superior Basin is 1.3 ng/L, while the human health-based standard applicable to waters outside the Lake Superior Basin is 6.9 ng/L. In addition to these numeric standards, Chapter 7050.0150, subpart 7, provides a narrative standard for assessing the contaminants in fish tissue. The narrative standard states that a waterbody is impaired when the Minnesota Department of Health recommends a consumption frequency of less than one meal per week for any member of the population.

To establish the two regional TMDLs, Minnesota selected a target of 0.2 mg/kg fish tissue mercury concentration. Fish tissue mercury concentration was selected as the water quality target for the TMDLs because it was consistent with EPA's 2001 methylmercury fish tissue criterion. In the 2001 guidance, EPA chose to express the water quality criterion as a fish tissue concentration rather than as a water column value because fish consumption is the primary route of human exposure. Two aspects of EPA's criterion are toxicity and exposure. Minnesota relied on EPA's assessments of toxicity to humans but selected a more state-specific exposure rate. For purposes of calculating its recommended human health-based fish tissue criterion, EPA assumes that people consume 17.5 g/day of fish. Minnesota selected a higher consumption rate, 30 g/day of fish, based on several surveys of the fish-eating habits of upper-Midwest recreational fishers.

Since Minnesota's water quality standards are water column chronic standards for total mercury, not fish tissue concentration standards, Minnesota demonstrated a link from the fish tissue mercury concentration TMDL target to the numeric water column water quality standards. Bioaccumulation factors for 14 lakes representing agricultural areas, urban areas, and forested areas were used to calculate the water column concentration that would be equivalent to the 0.2 mg/kg fish tissue mercury concentration target.

Source Assessment

Sources that Minnesota considered in developing the two regional TMDLs included atmospheric deposition, wastewater treatment plants, non-municipal waste discharges, and stormwater. Atmospheric deposition was the only significant nonpoint source of mercury identified by Minnesota. The state identified 99 percent of the total mercury load to the state as coming from atmospheric deposition. Both natural and anthropogenic

[27] As described in Section 6 of this guidance, Minnesota divided the state into two regions, a northeast region and a southwest region, and developed a TMDL for each region. Although Minnesota's report is called a "statewide TMDL," the two regional TMDLs do not address all the mercury impairments in the state. The TMDLs address 511 of the lake and river reach impairments in Category 5 of Minnesota's 2006 Integrated Report.

sources contribute to the atmospheric deposition mercury load. Minnesota identified natural sources as contributing 30 percent to the atmospheric deposition mercury load, while the remaining 70 percent is from worldwide anthropogenic sources. Point sources that Minnesota considered included wastewater treatment plants, pulp and paper mills, taconite mines, coal-fired power plants, and one refinery. The state recognized that stormwater is considered a point source and therefore subject to wasteload allocations; however, for purposes of estimating a baseline mercury load (referred to in the TMDL report as the total source load), the mercury loadings from stormwater were included in the estimate of loadings from atmospheric deposition. Using data from two studies in Minnesota, the state concluded that the primary source of mercury to stormwater is atmospheric deposition rather than specific anthropogenic sources.

Loading Capacity

Minnesota established a loading capacity for each of the two regional TMDLs. Each loading capacity was calculated by multiplying a regional reduction factor[28] needed to achieve the fish tissue mercury concentration target by the total source load[29] for each region, thus calculating a regional load reduction goal.[30] The load reduction goal was subtracted from the total source load to arrive at the loading capacities.

The total source load was considered the baseline condition from which reductions would be needed to achieve water quality standards. Minnesota selected the year 1990 as the baseline to which reductions would be applied. Minnesota selected 1990 as the baseline for three reasons. First, the total source load is the sum of the point source load and the nonpoint source load. The nonpoint source load is represented by total (wet and dry) mercury deposition. Minnesota's estimate of both wet and dry deposition is from lake sediment cores collected in a study conducted from 1988 to 1990. The second reason for selecting 1990 was to remain consistent with other mercury reduction baselines. The state uses 1990 as its mercury emission inventory baseline, and other state and federal plans, such as the Great Lakes Binational Toxics Strategy and the Lake Superior Lakewide Management Plan, use 1990 as a baseline for assessing mercury reductions. Minnesota selected a baseline year that was consistent with other reduction goals and targets. Last, Minnesota selected 1990 because prior to 1990 mercury use was relatively high, and then beginning in around 1990, mercury use dropped precipitously as mercury was removed from many products. For this reason Minnesota concluded that 1990 represents the end of a period when mercury emissions and fish tissue concentrations were in a steady state.

The sum of the point source load and nonpoint source load are the total source load for each region. The total source load for each region simply defines the 1990 baseline condition for the region to which the applicable reduction factor is applied.

The existing point source contribution to the total source load was calculated based on the sum of design flows for point sources within each region and mean effluent mercury concentrations. The design flows were current-day design flows, while the mean effluent

[28] The northeast regional reduction factor is 65 percent, and the southwest regional reduction factor is 51 percent.

[29] The baseline load for the northeast region is 1153 kg/yr, and the baseline load for the southwest region is 1628 kg/yr.

[30] The load reduction goal for the northeast region is 749 kg/yr, and the load reduction goal for the southwest region is 830 kg/yr.

mercury concentrations were "typical" mercury concentrations unless actual facility effluent concentrations were available. Actual facility effluent concentrations were used for the coal-fired power plants, the one refinery, and the Metro and Western Lake Superior Sanitary District wastewater treatment plants. For all other point sources, typical mercury concentrations were used. A typical effluent concentration of 5 ng/L was used for wastewater treatment plants. It was based on a study by the Association of Metropolitan Sewerage Agencies, a state study of 37 NPDES facilities, and the Mercury Maps report. Minnesota relied on the Mercury Maps report in support of the mean effluent mercury concentration of 13 ng/L for pulp and paper mills, although effluent reports from one Wisconsin and one Minnesota facility show effluent concentrations in the range of 1.6 ng/L to 2 ng/L. Minnesota used its discharge monitoring database to calculate 1.5 ng/L as the mean mercury effluent concentration for taconite mines.

The existing nonpoint source contribution to the total source load was based on total mercury deposition to the state. Minnesota used sediment cores from Minnesota lakes to estimate total statewide mercury deposition as 12.5 g km^{-2} yr^{-1}. Minnesota used the regional surface areas for each of the two regions, along with the total mercury deposition, to estimate the nonpoint source contribution to the total source load.

The reduction factor for each region is the percent reduction in total mercury load needed to achieve the fish tissue target of 0.2 mg/kg for the 90th percentile of the standard-length fish. Fish tissue data were reviewed for the standard-size top predator fish in each region. The 90th percentile fish tissue mercury concentration and median concentrations were calculated for each region for top predator fish (walleye and northern pike). Minnesota used the difference between the 90th percentile mercury concentration in top predator fish within each region and the 0.2 mg/kg target to calculate the reduction factors. Minnesota used fish tissue data from 1988 to 1992 to establish the reduction factors. The state looked at fish tissue data from 1970 to 2002; however, to be consistent with the baseline year of 1990, fish tissue data from 1988 to 1992 were selected. Multiyear data better represent real conditions over time because they account for year-to-year variability in weather, fish populations, and sampling locations. Data for the standard-size top predator fish were used to calculate the reduction factor. Mercury bioaccumulates in fish; therefore, mercury concentrations are typically highest in the top predator fish. To account for temporal and spatial comparisons of mercury concentrations in these top predator fish, Minnesota used the standard-size top predator fish.[31] Top predator fish that are collected for fish tissue analysis vary in size and age. Because mercury concentrations vary with the size of fish and age of fish, it is difficult to make comparisons regarding mercury concentrations in fish without establishing a standard of comparison. Use of the standard-size fish accounted for differences in mercury concentrations due to age and size and allowed Minnesota to compare mercury concentrations across waterbodies.

[31] Minnesota uses a standard size of 40 cm (approximately 22 inches) for walleye and 55 cm (approximately 16 inches) for northern pike.

Allocations

Consistent with the regional approach used to establish the loading capacities, Minnesota did not assign waterbody-specific allocations; rather, the state established gross allocations for each region.

Minnesota assigned 1 percent of the loading capacity to point sources as the wasteload allocation for each regional TMDL. Minnesota chose 1 percent of the loading capacity based on an approach used in the Mercury Maps report to screen watersheds for significant point source impacts to identify waterbodies impaired primarily by atmospheric mercury (see appendix E on Mercury Maps). The northeast region wasteload allocation was set at 1 percent of the loading capacity, while the southwest region's wasteload allocation was set equal to the point source load portion of the total source load. The state set the southwest region's wasteload allocation equal to the point source load portion of the total source load because it was slightly less than 1 percent of the southwest region's loading capacity and the state chose the more restrictive allocation.

Load allocations for each region were established by subtracting the wasteload allocation and any explicit margin of safety from the established loading capacity. The remaining load within each region was assigned to the load allocation. The approved loading capacity and allocations for both regional TMDLs are shown in table D13.

Table D13. Approved northeast and southwest mercury TMDLs

Region	Loading capacity	Load allocation	Wasteload allocation	Margin of safety
Northeast	1.10 kg/day	1.09 kg/day	0.01 kg/day	Implicit
Southwest	2.18 kg/day	1.55 kg/day	0.02 kg/day	0.61 kg/day

Appendix E. Model Descriptions

This appendix describes currently available models discussed in this guidance. These models aid in developing bioaccumulation factors and modifying fish tissue criteria (see chapter 3), making assessments (see chapter 4), developing total maximum daily loads (TMDLs) (see chapter 6), and in carrying out related programs such as 319 Nonpoint Source Program activities, watershed management, stormwater permits, and National Pollutant Discharge Elimination System (NPDES) discharge evaluations. This appendix provides a description of each model, some examples of how or where it has been used, and a Web site for further information about each model.

BASS (Bioaccumulation and Aquatic System Simulator)

The Bioaccumulation and Aquatic System Simulator (BASS) is a model that simulates the population and bioaccumulation dynamics of age-structured fish communities. Although BASS was specifically developed to investigate the bioaccumulation of chemical pollutants within a community or ecosystem context, it can also be used to explore population and community dynamics of fish assemblages that are exposed to a variety of non-chemical stressors such as altered thermal regimes associated with hydrological alterations or industrial activities, commercial or sports fisheries, and introductions of non native or exotic fish species.

BASS is being used to investigate methylmercury bioaccumulation in the Florida Everglades and to predict population and community dimensions of "fish health" for a regional analysis of the ecological sustainability of the Albemarle Pamlico drainage basin in North Carolina and Virginia.

Information on BASS can be found at: http://www.epa.gov/athens/research/modeling/bass.html.

Community Multi-Scale Air Quality (CMAQ) Model

The CMAQ modeling system is a comprehensive, three-dimensional, grid-based Eulerian air quality model designed to estimate pollutant concentrations and depositions over large spatial scales (Byun and Ching 1999; Byun and Schere 2006; Dennis et al. 1996). The CMAQ model is a publicly available, peer-reviewed, state-of-the-science model consisting of a number of science attributes that are critical for simulating the oxidant precursors and nonlinear chemical relationships associated with the formation of mercury. Version 4.3 of CMAQ (Bullock and Brehme 2002; Byun and Schere 2006) reflects updates to earlier versions in a number of areas to improve the underlying science and address comments from peer review. The updates in mercury chemistry in version 4.3 from that described in Bullock and Brehme (2002) are as follows:

1. The elemental mercury (Hg^0) reaction with H_2O_2 assumes the formation of 100 percent reactive gaseous mercury (RGM) rather than 100 percent particulate mercury (Hg_P).

2. The Hg^0 reaction with ozone assumes the formation of 50 percent RGM and 50 percent Hg_P rather than 100 percent Hg_P.

3. The Hg^0 reaction with OH assumes the formation of 50 percent RGM and 50 percent Hg_P rather than 100 percent Hg_P.

4. The rate constant for the Hg^0 + OH reaction was lowered from 8.7 to 7.7 x 10^{-14} cm^3 $molecules^{-1}s^{-1}$.

CMAQ simulates every hour of every day of the year and requires a variety of input files that contain information pertaining to the modeling domain and simulation period. These include hourly emissions estimates and meteorological data in every grid cell and a set of pollutant concentrations to initialize the model and to specify concentrations along the modeling domain boundaries.

Meteorological data, such as temperature, wind, stability parameters, and atmospheric moisture content influence the formation, transport, and removal of air pollution. The CMAQ model requires a specific suite of meteorological input files to simulate these physical and chemical processes. For recent CMAQ modeling, meteorological input files were derived from a simulation of the Pennsylvania State University's National Center for Atmospheric Research Mesoscale Model (Grell et al. 1994) for the entire year of 2001. This model, commonly referred to as MM5, is a limited-area, nonhydrostatic, terrain-following system that solves for the full set of physical and thermodynamic equations that govern atmospheric motions. For this analysis, version 3.6.1 of MM5 was used. A complete description of the configuration and evaluation of the 2001 meteorological modeling is provided by McNally (2003).

These initial and boundary concentrations were obtained from the output of a global chemistry model, Harvard's GEOS-CHEM model (Yantosca 2004), to provide the boundary concentrations and initial concentrations. The global GEOS-CHEM model simulates atmospheric chemical and physical processes driven by assimilated meteorological observations from NASA's Goddard Earth Observing System (GEOS). This model was run for 2001 with a grid resolution of 2 degrees x 2.5 degrees (latitude-longitude) and 20 vertical layers.

The CMAQ modeling domain encompasses all the lower 48 states and extends from 126 degrees west longitude to 66 degrees west longitude and from 24 degrees north latitude to 52 degrees north latitude. The modeling domain is segmented into rectangular blocks referred to as grid squares. The model predicts pollutant concentrations and depositions for each grid cell. For this application the horizontal domain consisted of 16,576 grid cells that are roughly 36 km by 36 km. The modeling domain contains 14 vertical layers, with the top of the modeling domain at about 16,200 meters, or 100 millibar. The height of the surface layer is 38 meters.

A CMAQ modeling run was performed to estimate the impact of global sources on U.S. deposition estimates. For this analysis, all non-U.S. mercury input species to the model were set to zero. By comparing the results of this analysis with the 2001 Clean Air Mercury Rule (CAMR) base case run, which included all U.S. and global mercury species, the percent of total mercury deposition attributable to global sources can be

estimated.[32] The model estimated that over 80 percent on average of total mercury deposition in the United States is attributable to global sources.

Due to the evolving nature of mercury modeling science, such deposition estimates have associated uncertainties. For example, it remains difficult to distinguish between the natural emissions of mercury and the re-emission of previously deposited anthropogenic mercury and there remains uncertainty in the scientific community concerning the atmospheric processes that control the oxidation state of atmospheric mercury. Thus, further advances in the current understanding of mercury chemistry could potentially lead to changes in the modeling parameters and assumptions governing the mercury chemistry in the models and therefore, changes in the estimate of the fraction deposited in the U.S. attributable to global sources.

For more information on CMAQ, see http://www.epa.gov/asmdnerl/CMAQ.

D-MCM (Dynamic Mercury Cycling Model)

D-MCM is a food web simulation of mercury accumulation in lakes. It predicts the cycling and fate of major forms of mercury in lakes, including methylmercury, Hg (II), elemental mercury, and total mercury. It is a time-dependent mechanistic model which considers the most important physical, chemical, and biological factors affecting fish mercury concentrations in lakes. D-MCM is meant for lotic (lake) systems, and is not meant to be used for lentic (streams, rivers, etc.) systems.

D-MCM can be used to develop and test hypotheses, scope field studies, improve understanding of cause and effect relationships, predict responses to changes in loading, and support design and evaluation of mitigation options. It was used in the development of mercury TMDLs for McPhee and Narraguinnep Reservoirs in Colorado and for the TMDLs for Arivaca and Pena Blanca Lakes in Arizona. The Everglades Mercury Cycling Model (E-MCM) was developed off of D-MCM and added vegetation processes and the ability to simulate multiple sediment layers for wetlands.

Information on D-MCM can be found at: http://rd.tetratech.com/DraftHgBrochurev2.pdf.

EXAMS2 (Exposure Analysis Modeling System)

EXAMS2 is a model for creating aquatic ecosystem models which can evaluate the fate, transport, and exposure concentrations of chemicals. Chemicals include synthetic organic chemicals like pesticides, industrial materials, and leachates from disposal sites. EXAMS2 core is a set of modules that link chemical properties to limnological characteristics that control the fate and transport of chemicals in aquatic systems. This model allows for both long-term analysis of chronic chemical discharges at constant release and varying release over time, and short-term analysis of chemical releases.

EXAMS2 has commonly been used to predict pesticide fate in water and soil. This model has been used to evaluate the role of hydroxyl radicals in degrading pesticides by

[32] On February 8, 2008, the D.C. Circuit Court of Appeals vacated the Clean Air Mercury Rule and remanded portions of it to EPA, for reasons unrelated to the technical analyses cited in this guidance.

researchers at the University of Georgia. EXAMS2 was also used to simulate mercury fate in the Withlacoochee River watershed and the Ohoopee River watershed in Georgia.

Information on EXAMS2 can be found at: http://www.epa.gov/ceampubl/swater/exams/.

GBMM (Grid Based Watershed Mercury Model)

EPA's Grid Based Watershed Mercury Model (GBMM) is a continuous grid-based watershed mercury loading model using the latest ArcGIS platform. It simulates the spatial and temporal dynamics of mercury from both point and non-point sources on a daily basis. The model calculates the water balance, sediment generation and transport, and mercury dynamics within a watershed. The mercury transport and transformation module simulates the following key processes:

- Mercury input from atmospheric deposition.
- Mercury assimilation and accumulation in forest canopy and release from forest litter.
- Mercury input from bedrock weathering.
- Mercury transformation in soils.
- Mercury transformation in lakes and wetlands including reduction and net methylation.
- Mercury transport through sediment and runoff.
- Mercury transport in stream channels.

GBMM accepts input data from atmospheric deposition, point sources, and natural background in time series or in digital spatial maps. By using the grid-based technology, flow and mercury dynamics can be examined at any of several points in the watershed.

The software has been peer reviewed and tested on two watersheds in Georgia, where it was used to calculate mercury TMDLs. GBMM has been used to investigate the mercury fate and transport in Brier Creek watershed located in the coastal plain of Georgia. GBMM was used to investigate detailed watershed mercury processes. The findings of this study were presented in Eighth International Conference on Mercury as a Global Pollutant (August 2006), Madison, Wisconsin, USA.

For more information on GBMM please visit: http://www.epa.gov/athens/research/modeling/mercury/gbmm.html.

GEOS-CHEM Model

The Global GEOS-CHEM model simulates physical and chemical atmospheric processes driven by observations by NASA's Goddard Earth Observing System (GEOS). This model is managed and supported by the atmospheric chemistry modeling group at Harvard University. This model is used as a tool for atmospheric composition problems.

This model was run for the 2001 CMAQ model with a grid resolution of 2 degree x 2.5 degree (latitude-longitude) and 20 vertical layers. GEOS–Chem is a major contributor to

the NASA Global Model Initiative (GMI). GEOS–Chem has been interfaced with the NASA/GISS general circulation model to investigate the effects of climate change. This work contributes to the multi-institutional Global Change and Air Pollution (GCAP) project. GEOS–Chem provides chemical modules for data assimilation of tropospheric composition at the NASA GMAO.

For more information on GEOS-CHEM please visit: http://www-as.harvard.edu/chemistry/trop/geos/geos_overview.html.

GWLF (Generalized Watershed Loading Function)

GWLF simulates mixed land use watersheds to evaluate the effect of land use practices on downstream loads of sediment and nutrients (N, P). As a loading function model, it simulates runoff and sediment transport using the curve number (CN) and Universal Soil Loss Equation (USLE), combined with average nutrient concentration, based on land use. Recently, a GIS-interface has been integrated which can use national land use and soil GIS data. Also GWLF models in-stream routing using the Muskingum-Cunge method and simulates three particle classes of sediment transport.

GWLF has been used in studies and TMDL development nationally. It is suitable for application to generalized watershed loading, source assessment, and seasonal and interannual variability. It has been extensively used in northeast and mid-Atlantic regions. It has been adopted by Pennsylvania as state system for TMDL development and agricultural land management. GWLF was used to calculate mercury load from the watershed to a lake in several TMDLs in Arizona (e.g., TMDL for Pena Blanca Lake, Arizona). GWLF is also applied in West Virginia TMDL projects by Tetra Tech, Inc.

Information on GWLF can be found at: http://www.epa.gov/nrmrl/pubs/600r05149/600r05149gwlf.pdf and http://www.vims.edu/bio/models/basinsim.html.

Mercury Maps screening analysis

A simple screening-level analysis of the mercury sources affecting a waterbody or waterbodies can assist in determining what type of approach to TMDLs is most appropriate. EPA's Mercury Maps (USEPA 2001b) is a geographic information system (GIS)-based analysis using national data coverage for watersheds, fish tissue concentrations, and non-air deposition source locations.

Mercury Maps uses a simplified form of the IEM-2M model applied in EPA's *Mercury Study Report to Congress* (USEPA 1997a). By simplifying the assumptions inherent in the freshwater ecosystem models described in the report to Congress, Mercury Maps showed that these models converge at a steady state solution for methylmercury concentrations in fish that are proportional to changes in mercury inputs from atmospheric deposition (e.g., over the long term, fish concentrations are expected to decline proportionally to declines in atmospheric loading to a waterbody). This analytical approach applies only to situations where air deposition is the only significant source of mercury to a waterbody and the physical, chemical, and biological characteristics of the ecosystem remain constant over time. To predict reductions in fish concentrations, Mercury Maps requires estimates of percent air deposition reductions by watershed, as

generated from a regional air deposition model, and georeferenced measurements of mercury concentrations in fish.

A state or authorized tribe can apply Mercury Maps on a state or watershed scale. For example, it could apply Mercury Maps on a statewide scale, using state- or tribe-defined watershed boundaries. The state might have its own data on point source effluent loads and more detailed information on other significant sources of mercury in the state, e.g., erosion of mine tailings or natural geology.

Because Mercury Maps is a simplified approach, it has several limitations.

1. The Mercury Maps approach is based on the assumption of a linear, steady state relationship between concentrations of methylmercury in fish and present-day air deposition mercury input. This condition might not be met in many waterbodies because of recent changes in mercury inputs and other environmental variables that affect mercury bioaccumulation. For example, the United States has recently reduced human-caused emissions, and international emissions have increased.

2. Environmental conditions might not remain constant over the time required to reach steady state inherent in the Mercury Maps methodology, particularly in systems that respond slowly to changes in mercury inputs.

3. Many waterbodies, particularly in areas of historical gold and mercury mining in western states, contain significant non-air sources of mercury. Mercury Maps' methodology should not be applied to such waterbodies.

4. Finally, Mercury Maps does not provide for a calculation of the time lag between a reduction in mercury deposition and a reduction in the methylmercury concentrations in fish.

Despite the limitations of Mercury Maps, for those watersheds where mercury comes almost exclusively from air deposition, Mercury Maps can be used as a simple screening tool to show the watersheds across a region where the current fish tissue concentration on average exceeds the new methylmercury fish tissue criterion and, thus, to estimate the atmospheric load reductions needed to meet the new criterion. Further information on Mercury Maps is at http://www.epa.gov/waterscience/maps and from the Office of Air Quality Planning and Standards at http://www.epa.gov/ttn/atw/utility/ria_final.pdf.

MOBILE

MOBILE is an EPA model for estimating air pollution from highway vehicles. MOBILE predicts emissions (grams/mile) of air pollutants from cars, trucks, and motorcycles under various conditions. MOBILE models emissions of several air toxics, hydrocarbons (HC), carbon monoxide (CO), oxides of nitrogen (NO_x), carbon dioxide (CO_2), and particulate matter (PM). MOBILE is based on emissions testing of tens of thousands of vehicles. The model accounts for the impact on emissions of factors such as legislative changes in vehicle emission standards, variation in local conditions such as temperature, humidity, and fuel quality, and changes in the types and use of the vehicles being driven.

MOBILE has been used to calculate national and local inventories of current and future levels of highway vehicle emissions. The inventories are used to inform decision-making

about air pollution policy and programs at the national, state and local level. Inventories based on MOBILE are also used to meet requirement of federal statutes like the Clean Air Act (CAA) and the National Environmental Protection Act (NEPA). MOBILE contributed to the creation of the National Emissions Inventory (NEI).

Information on MOBILE can be found at: http://www.epa.gov/otaq/mobile.htm.

NDMMF (National Descriptive Model of Mercury in Fish Tissue)

NDMMF is a statistical model which simulates mercury accumulation in varying species of fish. It simulates factors representing differences in species, size, and sampling method. This model has the ability to control for site factors specific to a location that influence mercury concentrations in fish tissue. For example, all fish tissue samples can be scaled to a standardized 14" bass for a specific location. The model works in association with a national dataset of over 30,000 samples of fish tissue for calibration.

NDMMF could be useful for evaluating spatial and temporal trends in fish mercury concentrations and developing fish-consumption advisories. The U.S. Geological Survey recently applied this model to study spatial variation in fish-tissue mercury concentrations in the St. Croix River Basin, Minnesota and Wisconsin.

Information on NDMMF can be found at: http://emmma.usgs.gov/fishHgAbout.aspx.

NONROAD

NONROAD is an EPA model for estimating air pollution from all engines, equipment, and vehicles that is considered "nonroad". This includes recreational vehicles, agricultural equipment, industrial equipment, residential equipment, and construction equipment. The NONROAD model is used to predict past, present, and future emissions of air pollutants like hydrocarbons (HC), oxides of nitrogen (NO_x), carbon monoxide (CO), carbon dioxide (CO_2), sulfur oxides (SO_x), and particulate matter (PM). It has been shown that "nonroad" sources contribute a significant amount of air pollutants to the environment.

Used in complement to MOBILE, NONROAD has been used to calculate national and local inventories of current and future levels of "nonroad" emissions. This model has become critical over the past several years in providing state and local pollution control agencies the ability to create accurate and consistent inventories of "nonroad" emissions to satisfy the requirements of the Clean Air Act Amendments of 1990. NONROAD contributed to the creation of the National Emissions Inventory (NEI). The Lake Michigan Air Directors Consortium (LADCO) used NONROAD to forecast emissions in their region and make appropriate policy recommendations.

Information on NONROAD can be found at: http://www.epa.gov/otaq/nonrdmdl.htm.

QEAFDCHN (Quantitative Environmental Analysis Food Chain) Model

The QEAFDCHN model is a tool for predicting chemical residues in aquatic organisms given the concentrations of chemicals in water and sediment. To predict chemical residues, the model requires information on the individual species (bioenergetic and physiological) and their diets. The model is designed to determine chemical residue in

aquatic organisms given varying chemical concentrations in both water and sediment over time.

The QEAFDCHN model can be used in a steady-state or dynamic application. The model allows the specification of complex food webs, e.g., fish preying on multiple species including smaller fish, and even age classes of fishes. The model treats individual segments of the greater ecosystem as individual ecosystems and the model has an aquatic organism migration feature. QEAFDCHN has been applied to the Lavaca Bay, Texas, chlor-alkali facility mercury contamination study by Quantitative Analysis, LLC.

Information on QEADFCHN can be found at: http://www.epa.gov/superfund//health/conmedia/sediment/pdfs/bsafissue.pdf.

Regional Modeling System for Aerosols and Deposition (REMSAD)

REMSAD is a three-dimensional grid model designed to calculate the concentrations of both inert and chemically reactive pollutants by simulating the physical and chemical processes in the atmosphere that affect pollutant concentrations (ICF International 2006). REMSAD has been peer-reviewed and is designed to support an understanding of the distributions, sources, and removal processes relevant to fine particles and other airborne pollutants, including soluble acidic components and several toxic species (mercury, cadmium, dioxin, polycyclic organic matter [POM], atrazine, and lead).

Mercury can be present in the atmosphere in both the gas and particulate phases. The mercury species included in REMSAD are Hg^0 (elemental mercury vapor), Hg^{2+} (divalent mercury compounds in gas phase), and Hg_P (divalent mercury compounds in particulate phase). These species represent the oxidation state of mercury, and the gas and particulate phases. The reactions in REMSAD, which are based on the studies of Lin and Pehkonen (1999) and other recently published studies, simulate the transfer of mercury mass from one of these states to another. REMSAD Version 8 uses the full Carbon Bond-V mechanism to simulate gas-phase photochemical processes in the atmosphere (micro-CB is still available as an option), and it also includes a chemical mechanism to calculate the transformations of mercury.

REMSAD simulates both wet and dry deposition of mercury. Wet deposition occurs as a result of precipitation scavenging. Dry deposition is calculated for each species based on land-use characteristics and meteorological parameters. REMSAD also includes algorithms for the reemission of previously deposited mercury (originating from anthropogenic and natural sources) into the atmosphere from land and water surfaces due to naturally occurring (e.g., microbial) processes.

REMSAD provides estimates of the concentrations and deposition of mercury and all other simulated pollutants at each grid location in the modeling domain. Post-processing can provide concentration averages and deposition totals for any subset of the time span of the simulation for any location within the domain.

The mercury treatment in REMSAD can be expanded to include additional, tagged mercury species. The Particle and Precursor Tagging Methodology (PPTM) feature allows the user to tag or track emissions from selected sources or groups of sources and

to quantify their contribution to mercury deposition throughout the modeling domain and simulation period.

The REMSAD model is capable of "nesting" one or more finer-scale subgrids within a coarser overall grid. This feature uses a fully interactive two-way nesting capability that permits high resolution over selected source and/or receptor regions of interest. The modeling system can be applied at scales ranging from a single metropolitan area to a continent containing multiple urban areas.

REMSAD has been used in identifying the sources contributing mercury deposition to a waterbody. In an EPA Wisconsin pilot project, REMSAD was used to input the air pollutant deposition results to aquatic models like the Mercury Cycling Model, to examine how mercury levels in fish might respond to potential changes in deposition. REMSAD has been used to develop TMDLs and determine strategies for addressing mercury and other air pollutant deposition. REMSAD was used in developing the mercury TMDL for the Coastal Bays and Gulf Waters of Louisiana (approved in 2005) and the mercury TMDLs for middle and south Georgia (approved in 2002).

Information on REMSAD can be found at: http://remsad.saintl.com/.

SERAFM (Spreadsheet-based Ecological Risk Assessment for the Fate of Mercury)

The SERAFM model is a spreadsheet-based risk assessment tool specifically designed for mercury contaminated ecosystems. SERAFM uses a steady-state simplifying assumption and includes a series of sequentially linked modules presented on separate spreadsheets. These modules include:

- Atmospheric deposition
- Watershed soil erosion
- Watershed mercury loading
- Waterbody solids balance
- Equilibrium partitioning (DOC complexation, solids partitioning)
- Mercury speciation
- Waterbody mercury calculations (historic sediment contamination, background, and remedial goal)
- Fish tissue concentrations
- Wildlife hazard quotients

The SERAFM model incorporates more recent advances in scientific understanding and implements an updated set of the IEM-2M solids and mercury fate algorithms that were described in the 1997 *Mercury Study Report to Congress* (USEPA 1997c).

For more information on SERAFM please visit: http://www.epa.gov/athens/research/modeling/mercury/serafm.html and http://www.epa.gov/nerl/news/forum2005/knightes.pdf.

TOXI5

TOXI5 is one of two submodels of WASP (Water Quality Analysis Simulation Model), the other being EUTRO5, which deals with eutrophication. TOXI5 is a sediment transport model which can also simulate the transport and transformation of chemicals. The transport of up to three types of sediment and up to three chemicals can be simulated. The chemicals may react independently or they may be linked with reaction yields which predict the fate of the interaction. Dissolved and sorbed chemical concentrations in the waterbody bed and overlying waters can be predicted using TOXI5.

TOXI5 was used to simulate the fate of mercury in the Ochlockonee Watershed in Georgia, to help develop mercury TMDLs for the Southeast U.S., and to evaluate the feasibility of dam release of water on the Nakdong River in Korea to mitigate frequent accidental spills of toxic chemicals.

For more information on TOXI5 please visit: http://smig.usgs.gov/cgi-bin/SMIC/model_home_pages/model_home?selection=wasp.

WASP (Water Quality Analysis Simulation Program)

The Water Quality Analysis Simulation Program (WASP) is a dynamic compartment-modeling program for aquatic systems, including both the water column and the underlying benthos. It has detailed mercury transformation processes for the water column and benthic sediments. The mercury module simulates the following key processes:

- Volatilization of Hg^0 (aq) to Hg^0 (air)
- Oxidation of $Hg^0 \rightarrow Hg^{II}$
- Reduction of $Hg^{II} \rightarrow Hg^0$
- Methylation of HgII → MeHg
- Demethylation of MeHg → Hg^{II}
- Photoreduction of MeHg → Hg^0

WASP has been used to examine eutrophication of Tampa Bay, Florida; phosphorus loading to Lake Okeechobee, Florida; eutrophication of the Neuse River Estuary, North Carolina; eutrophication of the Coosa River and Reservoirs, Alabama; PCB pollution of the Great Lakes; eutrophication of the Potomac Estuary; kepone pollution of the James River Estuary; volatile organic pollution of the Delaware Estuary; heavy metal pollution of the Deep River, North Carolina; and mercury in the Savannah River, Georgia.

Information on WASP can be found at: http://www.epa.gov/athens/research/modeling/wasp.html.

WCS (Watershed Characterization System) Mercury Loading Model

The WCS Mercury Loading model is a GIS-based (ArcView 3.x) extension of the WCS model based on a soil-mercury mass balance model (IEM v 2.05). The soil-mercury mass balance model calculates surface soil concentrations in dissolved, sorbed, and gas phases.

The model accounts for three routes of contaminant entry into the soil:

- Deposition of particle-bound contaminant through dry fall
- Deposition through wet fall
- Diffusion of gas phase contaminant into the soil surface

The model also accounts for four dissipation processes that remove mercury from the surface soils:

- Volatilization (movement of gas phase out of the soil surface)
- Runoff of dissolved phase from the soil surface
- Leaching of dissolved phase through the soil horizon
- Erosion of particulate phase from the soil surface

The model assumes that the diffusion and volatilization processes are roughly balanced on an annual basis. The WCS Mercury Loading model was used to develop many TMDLs in EPA Region 4 including a mercury TMDL for the Middle and Lower Savannah River.

Information on the WCS model can be found at: http://www.epa.gov/athens/wwqtsc/WCS-toolbox.pdf.

Example of Linking Models

Since there is no single model that can simulate all processes involved in TMDLs, some TMDLs for mercury have linked together models of atmospheric deposition, watershed loading, and mercury cycling with bioaccumulation. For example, a watershed mercury model such as GBMM, or the watershed module within SERAFM could be linked to a receiving water mercury model such as WASP, and a bioaccumulation model such as BASS.

GBMM is a spatially discrete, dynamic watershed mercury loading model which was designed for direct linkage to the EPA receiving waterbody model, WASP. GBMM can simulate mercury fate and transport within the watershed landscape and transport mercury and soils to the receiving waters through the tributaries. WASP can in turn simulate mercury dynamics in the receiving water. To predict bioaccumulation of the resulting mercury concentrations into fish tissues, WASP can then be linked to BASS. SERAFM is a more simplified approach and captures the processes from watershed to waterbody to fish bioaccumulation; however, it makes simplifying assumptions such as the waterbodies are steady state and it uses the national BAFs presented by EPA for trophic level fish.

Linkage of such models may be a workable solution in some situations. One of the limitations of the GBMM-WASP-BASS approach is that it is not an “off-the-shelf” model and a high level of expertise might be required to link the models together.

Appendix F. Examples of National Deposition Monitoring Networks

A number of national deposition monitoring networks might be useful for developing TMDLs. The networks include the National Atmospheric Deposition Program–National Trends Network (NADP/NTN) and the Mercury Deposition Network (MDN, a subset of the NADP network). The NADP/NTN is a nationwide network of precipitation monitoring stations. Operating since 1978, it collects data on the chemistry of precipitation for monitoring of geographic patterns and temporal long-term trends. NADP/NTN measures weekly average concentrations of sulfate, nitrate, ammonium, base cations, and acidity at approximately 230 monitoring stations across the United States. The MDN measures concentrations of total mercury in precipitation at approximately 45 monitoring stations across the United States and Canada. NADP/NTN results for 2003 are shown in figure F-1. For more information about NADP, see http://nadp.sws.uiuc.edu.

Used in conjunction with NADP/NTN, the Clean Air Status and Trends Network (CASTNET) is the nation's primary source of atmospheric data on the dry deposition component of total acid deposition, ground-level ozone, and other forms of atmospheric pollution that enters the environment as particles and gases. CASTNET measures weekly average atmospheric concentrations of sulfate, nitrate, ammonium, sulfur dioxide, and nitric acid, as well as hourly concentrations of ambient ozone levels in rural areas. Dry deposition rates are calculated using the measured atmospheric concentrations, meteorological data, and information on land use, surface conditions, and vegetation. Seventy-nine monitoring stations operate across the United States. For more information about CASTNET, see http://www.epa.gov/castnet and http://nadp.sws.uiuc.edu.

Note that these national monitoring networks generally provide only estimates of wet deposition; estimates of dry deposition can be obtained from the literature. For more information on deposition monitoring networks, see *Deposition of Air Pollutants to the Great Waters: Third Report to Congress* (USEPA 2000h) (http://www.epa.gov/oar/oaqps/gr8water/3rdrpt) and the Air-Water Interface Plan (http://www.epa.gov/ttn/caaa/t3/reports/combined.pdf).

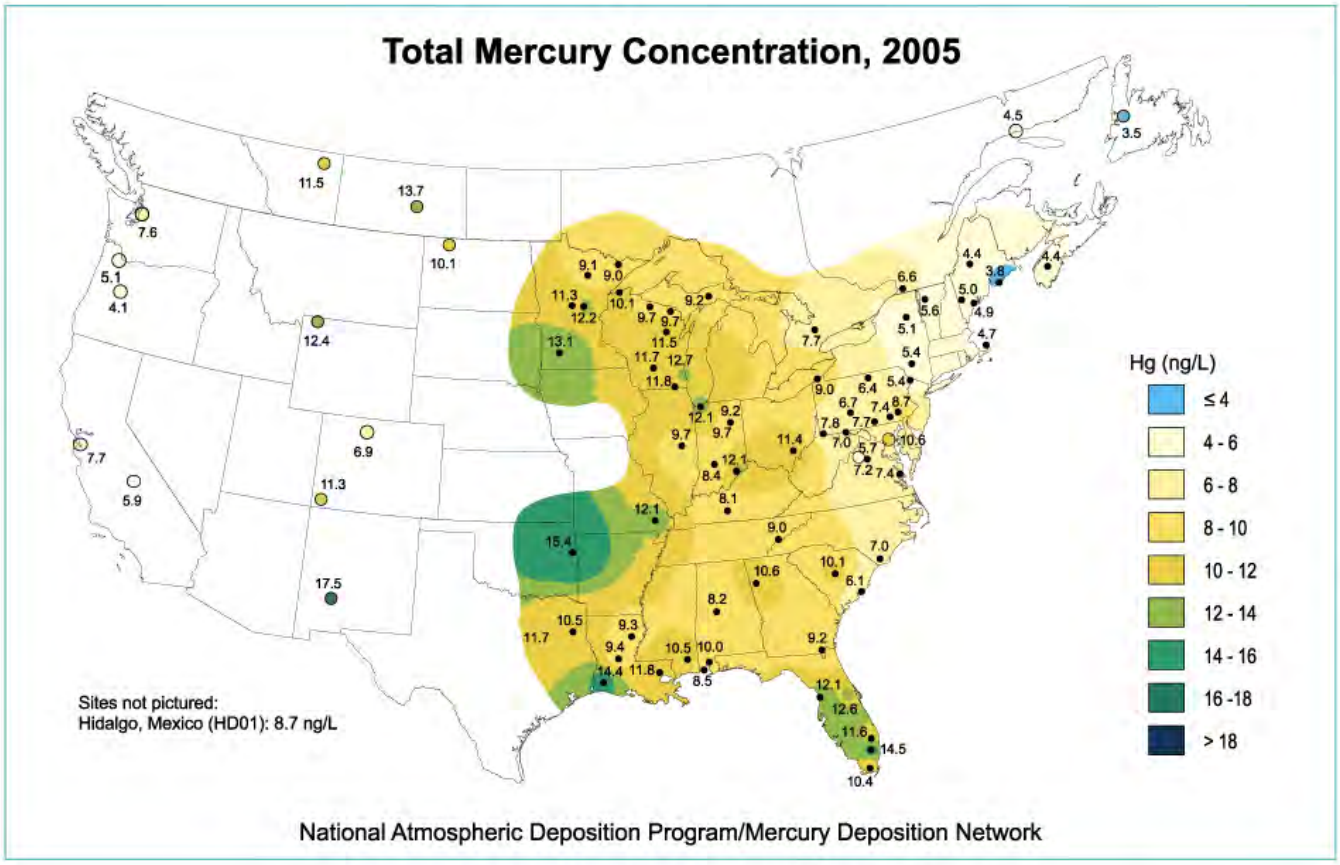


Figure F-1. MDN data for 2005.

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Note: Bold numbers indicate where the term is defined (if applicable). If the term has been broken into subcategories, this is noted with a *defined* entry.

U.S. Department of the Interior
Fish and Wildlife Service

Evaluation of the Clean Water Act Section 304(a) Human Health Criterion for Methylmercury: Protectiveness for Threatened and Endangered Wildlife in California

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EXECUTIVE SUMMARY

Introduction

In January 2001, the U.S. Environmental Protection Agency (EPA) developed a new recommended water quality criterion for methylmercury, under section 304(a) of the federal Clean Water Act. The criterion, a tissue residue concentration (TRC) of 0.3 milligrams per kilogram wet weight (mg/kg, ww) of methylmercury in edible portions of fish and shellfish, was designed to protect human health against adverse effects of methylmercury toxicity. The EPA intends to propose this human health criterion in California in order to fulfill consultation obligations under the federal Endangered Species Act (ESA) stemming from promulgation of the California Toxics Rule in 2000. As part of that ESA consultation, the EPA agreed that the human health criterion should be sufficient to protect federally listed aquatic and aquatic-dependent wildlife species in California. In proposing this criterion, the EPA must complete a biological evaluation of the effects of the proposed action on federally listed and proposed threatened and endangered species and critical habitat within California.

To facilitate this biological evaluation, the EPA's Region 9 entered into an Intergovernmental Agreement (IAG) with the U.S. Fish and Wildlife Service's (Service) Sacramento Fish and Wildlife Office, Environmental Contaminants Division (ECD). The primary objective of this IAG was to conduct the analyses necessary to determine whether the TRC may affect any federally listed species in California. This document presents the risk assessment methodology, developed collaboratively by scientists from both the Service and EPA, used to perform these analyses. This document also provides the ECD's interpretation of the results and our conclusions regarding the TRC's effect on the species evaluated. **These conclusions do not represent the results of consultation under Section 7 of the ESA, rather they were based solely on our current understanding of methylmercury's behavior in aquatic ecosystems and the toxicological foundation from which the risk assessment methodology was developed.** The results of these analyses may be used by the EPA in making ESA-related effects determinations for the subsequent biological evaluation. Any such determinations are solely the responsibility of the EPA.

Evaluating Wildlife Protection

The 0.3 mg/kg TRC represents a generic dietary concentration intended to be the maximum allowable concentration of methylmercury in freshwater and estuarine fish and shellfish that would protect human consumers, based on an average consumption of 17.5 grams of fish and shellfish per day. It is possible to develop similar dietary concentrations for wildlife species, provided sufficient life history and toxicity data exist. However, the protection of wildlife cannot be evaluated by simply comparing a protective generic dietary concentration determined for any given species with the generic dietary concentration proposed as the human health criterion.

One of the primary principles in constructing a risk assessment to evaluate wildlife protection is the need to consider the food chains of aquatic ecosystems in terms of trophic levels. Food chains, defined in their most simplistic form, start with trophic level 1 (TL1) plants. These plants are consumed by trophic level 2 (TL2) herbivores, which are consumed by trophic level 3 (TL3) predators, which are then consumed by the top predators in trophic level 4 (TL4). Consideration of trophic levels is necessary because methylmercury is a highly bioaccumulative pollutant which concentrates in biological tissues and biomagnifies as it moves up through successively higher trophic levels of a food chain. Organisms higher on the food chain contain greater methylmercury concentrations than those lower on the food chain. If fish and shellfish from TL2 contain tissue methylmercury concentrations of 0.3 mg/kg, then biota from TL3 and TL4 will have higher tissue concentrations. Conversely, if TL4 biota have tissue concentrations of 0.3 mg/kg, biota from TL2 and TL3 will have lower tissue concentrations.

There are numerous challenges in taking a trophic level approach to evaluating the TRC for its protectiveness of multiple listed fish and wildlife species. Most predators that feed from aquatic food webs are opportunistic and will consume prey from more than one trophic level. These dietary habits vary widely among different species and can change seasonally. Thus, methylmercury concentrations in any trophic level that may be protective of one species may place another consumer from the same water body at increased risk. In addition, different species of wildlife vary in their sensitivity to methylmercury toxicity. Since the toxicological literature contains dosing studies from very few species of wildlife, most ecological risk assessment methodologies, including this one, use uncertainty factors to account for unknown variations in sensitivity among species.

Consideration of these food chain dynamics in a risk assessment for wildlife requires trophic level-specific methylmercury concentrations. The manner in which the TRC is to be implemented for protection of human health will determine the limiting concentrations of methylmercury in the various trophic levels. Under a strict interpretation of the criterion (*i.e.*, no fish tissue exceeding the TRC), and given an understanding of biomagnification relationships between trophic levels, it is possible to set the TRC as the limiting concentration for TL4 biota and then estimate the tissue concentrations expected for biota in TLs 2 and 3. However, if a specific human population consumes only TL2 or TL3 fish from a water body, then the TRC could be applied to just those trophic levels. This would result in methylmercury concentrations in TL4 biota that are higher than the TRC and increase the exposure risks for wildlife.

For this evaluation, two approaches were used to determine trophic level-specific methylmercury concentrations that could be expected from the TRC. The Average Concentration TL Approach estimated these concentrations based on the human consumption rate of 17.5 g per day, with a defined trophic level composition (*i.e.*, a certain percentage from each trophic level). The Highest TL Approach set the TRC as the limiting concentration for TL4 biota, and then estimated the subsequent concentrations for TLs 2 and 3. Both approaches required assumptions about the relationships of bioaccumulation and biomagnification between trophic levels.

Average Concentration Trophic Level Approach

This approach estimated the methylmercury concentrations in each trophic level consumed by humans that, when combined, would correspond to the overall dietary concentration of 0.3 mg/kg. The EPA's human health methylmercury criterion document presented a national average intake rate of 17.5 grams of fish per day based on an assumed percentage from each individual trophic level: TL2 - 21.7% (3.8 g), TL3 - 45.7% (8.0 g), TL4 - 32.6% (5.7 g), for a total of 100% (17.5 g).

Based on national bioaccumulation data, it was determined that methylmercury concentrations in TL4 biota are generally 4.0 times those seen in TL3 biota. Concentrations in TL3 biota are generally 5.7 times those seen in TL2 biota. Using these methylmercury biomagnification factors and the assumed trophic level composition of the average human diet, the concentration of methylmercury in TL2, TL3, and TL4 fish and shellfish that will maintain an overall human dietary concentration of 0.3 mg/kg methylmercury can be calculated. The resulting concentrations are: TL2 - **0.029 mg/kg**; TL3 - **0.165 mg/kg**; and TL4 - **0.660 mg/kg**.

Highest Trophic Level Approach

This approach would set the proposed TRC of 0.3 mg/kg as the limiting concentration in TL4 biota. Concentrations expected in TLs 2 and 3 were then estimated by dividing by the appropriate biomagnification factors (*i.e.*, TL3 = TL4 concentration divided by 4, TL2 = TL3 concentration divided by 5.7). The resulting concentrations are: TL4 - **0.3 mg/kg**, TL3 - **0.075 mg/kg**; and TL2 - **0.013 mg/kg**.

This approach is the most conservative (*i.e.*, protective) method of establishing trophic level concentrations with the TRC. This is because it eliminates the possibility of different human populations exceeding the protective reference dose, assuming the national average consumption rate remains constant. Thus, a diet of 100 percent TL4 fish would maintain the overall dietary concentration of 0.3 mg/kg. Any other combination of trophic level foods in the diet (totaling 17.5 g per day) will maintain a dietary concentration at or below the protective level.

The trophic level methylmercury values for the two approaches were then used, along with dietary intake information for each species of concern, to evaluate the protectiveness of the TRC for aquatic and aquatic-dependent wildlife species at greatest risk from exposure to methylmercury.

Selection of Species

Based on the information available in the scientific literature, and given consideration of methylmercury's capacity to bioaccumulate and biomagnify in the aquatic food chain, this evaluation assumed that upper trophic level wildlife species (*i.e.*, predatory birds and mammals)

have the greatest inherent risk from exposure to methylmercury. In California these species are:

Southern Sea Otter (*Enhydra lutris nereis*)
California Least Tern (*Sterna antillarum brownii*)
California Clapper Rail (*Rallus longirostris obsoletus*)
Light-Footed Clapper Rail (*Rallus longirostris levipe*)
Yuma Clapper Rail (*Rallus longirostris yumaensis*)
Western Snowy Plover (*Charadrius alexandrinus nivosus*)
Bald Eagle (*Haliaeetus leucocephalus*)

The scientific literature was also reviewed to see whether the listed fish, reptile, and amphibian species may be protected under either trophic level approach. For fish species, the risk assessment was based solely on adverse effects associated with tissue methylmercury concentrations. The scientific literature contains little information on methylmercury risk to reptiles and amphibians.

Wildlife Values and Predicted Dietary Concentrations

A Wildlife Value (WV) represents the overall dietary concentration of methylmercury necessary to keep the daily ingested amount at or below a level at which no adverse effects are expected. The WV is analogous to the TRC for the human health criterion. For each species of concern, a WV was determined using body weight, total daily food ingestion rate, and a protective reference dose.

A predicted dietary concentration (DC) also represents an overall concentration in the diet, but is determined using the trophic level methylmercury concentrations expected under each TL approach and the trophic level composition of the species' diet. In effect, the percentage of each trophic level consumed is multiplied by the concentration expected for that trophic level. The resulting products are then summed to provide the total concentration of methylmercury in the diet.

The predicted DC for each species of concern was then compared to the WV determined to be protective for that species. If the predicted DC was at or below the WV then it was assumed that the species is not at risk from dietary exposure to methylmercury under that scenario. If the predicted DC is higher than the WV, it was assumed that the species would likely have a dietary exposure that may place it at risk for adverse effects from methylmercury toxicity.

Results of the Evaluation

Average Concentration Trophic Level Approach

Based on the analyses conducted for this evaluation, applying the TRC with the estimated trophic level methylmercury concentrations under the Average Concentration TL Approach may be

sufficiently protective for only two of the seven species considered: southern sea otter and Western snowy plover. **The five other species examined (California least tern; California, light-footed, and Yuma clapper rails; bald eagle) would likely have dietary exposures under this approach that may place them at risk for adverse effects from methylmercury toxicity**.

Highest Trophic Level Approach

This approach, with its lower estimated trophic level methylmercury concentrations, would provide a greater degree of protection than the Average Concentration TL Approach. Applying the TRC under the Highest TL Approach should be sufficiently protective for four of the seven species considered: southern sea otter, California clapper rail, Western snowy plover, and bald eagle. **Two of the species examined (California least tern and Yuma clapper rail) would likely have dietary exposures under this approach that may place them at risk for adverse effects from methylmercury toxicity**. The least tern may be at an elevated risk for methylmercury toxicity because of its small body size and its diet of exclusively TL3 fish. Although methylmercury concentrations for all three trophic levels are expected to be substantially lower under this approach, the estimated TL3 concentration of 0.075 mg/kg would still not be low enough to remove the potential risk of adverse effects from dietary methylmercury exposure for the least tern. The evaluation for the Yuma clapper rail, regardless of the WV used in the analysis, indicates this subspecies would likely have a dietary exposure under this approach that may place it at risk for adverse effects from methylmercury toxicity.

At this time, no conclusion can be drawn regarding the light-footed clapper rail. If this subspecies' sensitivity to methylmercury is the same as the California clapper rail and the analysis of its dietary composition is correct, the light-footed rail would likely have dietary exposures under this approach that may place them at risk. However, if other biological characteristics (*e.g.*, a greater ability to detoxify ingested methylmercury, lower diet-to-egg transfer efficiency) indicate a lower sensitivity to methylmercury, the evaluation results suggest this TL approach should be sufficiently protective for the light-footed rail. Research should be initiated to answer questions surrounding the relative sensitivity of this subspecies and to determine the appropriate trophic level methylmercury concentrations to provide sufficient protection against toxicity.

Fish

None of the data examined provided definitive answers regarding the level of protection for fish afforded by the TRC. **The methylmercury concentrations expected from applying the TRC under both trophic level approaches appear to be well below observed adverse effects concentrations; however, the trophic level concentrations expected under the Average TL Approach are much closer to these adverse effects concentrations.** Increasing emphasis on examining more subtle methylmercury-induced effects may reveal even lower tissue-based threshold effects concentrations for fish.

Reptiles and Amphibians

Too little is presently known about mercury bioaccumulation in reptiles and amphibians to allow for any comparative risk prediction capability based on bioaccumulation in fish. **The available scientific literature strongly suggests that both reptiles and amphibians can bioaccumulate methylmercury, although possibly less so than piscivorous birds and mammals with a greater daily reliance on aquatic prey. Until the appropriate toxicological data are generated, no definitive conclusions can be drawn about the protectiveness of either trophic level approach for the California red-legged frog, San Francisco garter snake, or giant garter snake.**

Discussion

The Service's Environmental Contaminants Division believes the analyses presented in this document represent the most current state of knowledge regarding the risk to California's listed species from dietary methylmercury. Conclusions about the protectiveness of the TRC for each species evaluated by the two trophic level approaches are summarized in Executive Summary (ES) Table 1. Of the two approaches evaluated, the Highest TL Approach affords a greater degree of protection for California's listed bird and mammal species than the Average TL Approach. The best currently available data on mercury toxicity in fish suggest that the TRC under either approach should be sufficiently protective of all listed fish in California; however, the trophic level concentrations expected under the Average TL Approach would be much closer to observed adverse effects concentrations described in the scientific literature. Although a lack of relevant data precludes any conclusions regarding the potential impact of the TRC on the reptile and amphibian species considered, the lower trophic level concentrations expected under the Highest TL Approach would afford a greater measure of protection than those expected under the Average TL Approach. **We believe that the TRC would not adequately protect all listed species in California; however, applying the TRC under the Highest TL Approach would reduce the number of species at risk.**

These conclusions reflect the interpretation of the evaluation results by the Service's Environmental Contaminants Division only, and are not intended to represent the views of those EPA or Service scientists who helped develop the risk assessment methodology. In addition, these conclusions do not constitute the results of consultation under Section 7 of the ESA.

Finally, it must be noted that the risk assessment methodology presented in this document was not applied to any wildlife species other than the federally listed species. Other non-listed wildlife may be potentially at risk under the TRC, due to their dietary dependence on aquatic ecosystems. **Using the same approach followed in this effort, regulatory agencies should be able to determine whether concentrations of methylmercury in fish tissue under the TRC may also pose a risk to non-listed wildlife species.**

ES Table 1. Protectiveness of EPA's Methylmercury Tissue Residue Criterion for Seven Federally Listed Califomia Species.

Is the TRC Protective for...	Southern Sea Otter	Ca. Least Tern	Ca. Clapper Rail	Light-footed Clapper Rail	Yuma Clapper Rail	Western Snowy Plover	Bald Eagle
Under the Average TL Approach?	Yes	**No**	Yes	**No**	**No**	Yes	**No**
-with interspecies uncertainty factor of 3*	na	na	**No**	**No**	**No**	Yes	na
Under the Highest TL Approach?	Yes	**No**	Yes	Yes	**No**	Yes	Yes
-with interspecies uncertainty factor of 3*	na	na	Yes	**No**	**No**	Yes	na

(na - not applicable)

* - discussion of uncertainty is presented in Section III.D. of document

I. INTRODUCTION

I.A. Background

In January 2001, the U.S. Environmental Protection Agency (EPA) developed a new recommended water quality criterion for methylmercury, under section 304(a) of the federal Clean Water Act (CWA; 33 U.S.C. 1251 - 1376, as amended). The criterion, a tissue residue concentration (TRC) of 0.3 milligrams per kilogram wet weight (mg/kg, ww) of methylmercury in edible portions of fish and shellfish, was designed to protect human health against adverse effects of methylmercury toxicity. In order to fulfill consultation obligations under the federal Endangered Species Act (ESA; 16 U.S.C. 1531-1544, as amended) stemming from promulgation of the California Toxics Rule in 2000, the EPA intends to propose this criterion in the State of California. While EPA intends to propose this TRC as a human health criterion, the Agency agreed as part of the California Toxics Rule ESA consultation that the human health criterion should be sufficient to protect federally listed aquatic and aquatic-dependent wildlife species. As part of the proposal process, the EPA must complete a biological evaluation of the effects of the proposed action on federally listed and proposed threatened and endangered species (see Appendix) and critical habitat within California.

To facilitate this biological evaluation, the EPA's Region 9 entered into an Intergovernmental Agreement (IAG) with the U.S. Fish and Wildlife Service's (Service) Sacramento Fish and Wildlife Office, Environmental Contaminants Division (ECD). The primary objective of this IAG was to conduct the analyses necessary to determine whether the TRC may affect any federally listed species in California. This document presents the risk assessment methodology, developed collaboratively by scientists from both the Service and EPA, used to perform these analyses. The results of these analyses may be used by the EPA in making ESA-related effects determinations for the subsequent biological evaluation. Any such determinations are solely the responsibility of the EPA. However, this document also provides the ECD's interpretation of the analytical results and our conclusions regarding the TRC's effect on the species evaluated. These conclusions do not represent the results of consultation under Section 7 of the ESA, rather they were based solely on our current understanding of methylmercury's behavior in aquatic ecosystems and the toxicological foundation from which the risk assessment methodology was developed.

I.B. Evaluating Wildlife Protection

When sufficient methylmercury toxicity data exist to determine a dietary dose at which no adverse effects to an organism are expected, then it becomes a relatively simple process to calculate a protective methylmercury concentration in the overall diet, based on information about that organism's body weight and daily food consumption. The 0.3 mg/kg[1] TRC represents just such a generic dietary concentration for humans. The TRC is intended to be the maximum

[1] All concentrations are reported on a wet weight basis unless otherwise noted.

allowable concentration of methylmercury in freshwater and estuarine fish and shellfish that would protect human consumers, based on an average consumption of 17.5 grams of fish and shellfish per day.

However, the protection of wildlife cannot be evaluated by simply comparing a protective generic dietary concentration determined for any given species with the generic dietary concentration proposed by the human health criterion. One of the primary principles in constructing a risk assessment methodology to evaluate wildlife protection was the need to consider aquatic ecosystems in terms of trophic levels. Trophic levels are general classifications applied to the various biotic components of a food chain, and organisms are placed in these classifications depending on what they consume. Stated in its most simplistic form, trophic level 1 plants are consumed by trophic level 2 herbivores, which are consumed by trophic level 3 predators, which are then consumed by the top predators in trophic level 4. Predator-prey relationships in real-world ecosystems are generally more complex than this simple linear model, with a tendency for higher order predators to include prey from more than one trophic level in their diets. However, the risk assessment methodology employed in this evaluation was based on the assumption that the general concepts underlying the simple linear food chain model remain a valid approach for considering the trophic transfer of methylmercury in aquatic biota. Trophic levels used in this evaluation were based on definitions provided in Volume I of *Trophic Level and Exposure Analyses for Selected Piscivorous Birds and Mammals* (U.S. Environmental Protection Agency, 1995a):

Trophic Level 1 - Plants and detritus
Trophic Level 2 - Herbivores and detritivores
Trophic Level 3 - Predators on trophic level 2 organisms
Trophic Level 4 - Predators on trophic level 3 organisms

This consideration of trophic levels was necessary because methylmercury is a highly bioaccumulative pollutant which concentrates in biological tissues and biomagnifies as it moves up through successively higher trophic levels of a food chain. The TRC was not derived by assuming specific methylmercury concentrations in any particular trophic level. Instead, 0.3 mg of methylmercury per kg of fish and shellfish tissue in a daily consumed average of 17.5 g was assumed to be protective for human populations eating from various trophic levels, rather than from any particular trophic level. However, due to the characteristics of methylmercury described above, aquatic food chains do not attain a steady-state condition wherein aquatic biota from all trophic positions exhibit the same tissue concentrations. Instead, organisms higher on the food chain contain greater concentrations than those lower on the food chain. For example, if fish and shellfish from trophic level 2 (*e.g.*, herbivorous fish) contain concentrations of 0.3 mg/kg, then biota from trophic levels 3 and 4 (*e.g.*, predatory fish) will undoubtedly have higher tissue concentrations. Conversely, if aquatic biota from the highest trophic level in the system have tissue methylmercury concentrations of 0.3 mg/kg, examination of lower order biota will show substantially lower tissue concentrations. Consideration of methylmercury's propensity to bioaccumulate and biomagnify as it is passed up the aquatic food chain was critical in this

evaluation as many higher order predators (*e.g.*, piscivorous birds and mammals) eat aquatic biota from a variety of trophic levels.

There are several challenges in evaluating the TRC for its protectiveness of multiple listed fish and wildlife species. The first involves determining the dietary characteristics of the species of concern (*e.g.*, ratio of daily food ingestion rate to body weight; trophic level composition of diet). Most predators that feed from aquatic food webs are opportunistic and will consume prey from more than one trophic level. Furthermore, the distribution of prey types they consume may vary seasonally. While an overall dietary methylmercury concentration can be calculated that will protect any given species, the amount of prey consumed from each trophic level is the driving factor influencing the amount of methylmercury ingested on a daily basis. The methylmercury concentration in the overall diet for any species is dependent on both the trophic level composition of its diet *and* the methylmercury concentrations in each of the trophic levels from which the species feeds. Without an understanding of this dietary composition, it is impossible to determine the limiting concentrations for each trophic level that will result in any calculated overall dietary concentration.

A second challenge is that these dietary characteristics vary widely from species to species. While one species may eat primarily from trophic level 2, another may prey predominantly on higher trophic level organisms. Methylmercury concentrations in any trophic level that may be protective of one species may place another consumer from the same water body at increased risk.

Another challenge is due to the potential for different species of wildlife to vary in their sensitivity to methylmercury toxicity. The toxicological literature contains dosing studies from very few species of wildlife, so most ecological risk assessment methodologies, including this one, use uncertainty factors to account for unknown variations in sensitivity among species. This is discussed in more detail in Section III.D., below.

In addition to the complexities of wildlife diets, another challenge involves how the TRC is to be implemented for protection of human health. Under a strict interpretation of the criterion (*i.e.*, no fish tissue exceeding the TRC), and given an understanding of biomagnification relationships between trophic levels, it may be possible to set the TRC for trophic level 4 biota and then estimate the tissue concentrations expected for biota in trophic levels 2 and 3. If the aforementioned dietary characteristics can be determined, the various trophic level methylmercury concentrations can then be used to evaluate their protectiveness for any given species. However, in implementing the criterion, adjustments may be made to account for site-specific or regional conditions regarding human consumption of fish and shellfish. These adjustments could include apportioning a fish intake rate to the highest trophic level consumed for a specific human population. This suggests that if a specific human population consumes only trophic level 2 or 3 fish from a water body, then the TRC could be applied to those trophic levels. The increased methylmercury concentrations in higher trophic levels resulting from this implementation could then increase the exposure for top wildlife predators.

II. APPROACHES TO EVALUATION

In order to evaluate the protectiveness of any given criterion expressed as a general concentration in the overall diet of a consumer eating from various trophic levels, it is first necessary to establish concentrations specific to each trophic level. As noted above, it is possible to set the human health criterion as the limiting concentration at trophic level 2, 3 or 4, depending on the particular fish consumption habits of the human population to be protected. Alternatively, varying concentrations in each trophic level could be calculated based on different combinations of the human dietary trophic level composition (*e.g.*, 90% trophic level 4 and 10% trophic level 3 vs. 50% trophic level 4, 40% trophic level 3, and 10% trophic level 2). Although a multitude of trophic level approaches are possible, this evaluation is focused on two options, each described below.

II.A. Average Concentration Trophic Level Approach

In the human health criterion development, the TRC was determined using a national average fish consumption rate of 17.5 g/day for the general population. This national average can be broken out by determining the percentage of fish and shellfish consumed from each of the three trophic levels (TL2, TL3, TL4). A trophic level breakout was presented in the human health criterion document, although this was not intended to be used in setting concentration limits for each trophic level. However, using this breakout to estimate individual trophic level concentrations that would maintain the overall dietary concentration of 0.3 mg/kg provides one way to evaluate the protectiveness of the TRC for species of concern. The following methodology describes the steps for conducting this approach.

The first step is to estimate the methylmercury concentrations in each trophic level consumed by humans that, when combined, would correspond to the overall dietary concentration of 0.3 mg/kg. In order to do this, several input parameters must first be identified:

%TL2 - Percent of trophic level 2 biota in diet
%TL3 - Percent of trophic level 3 biota in diet
%TL4 - Percent of trophic level 4 biota in diet
MTL3 - Food chain multiplier from TL2 to TL3 biota
MTL4 - Food chain multiplier from TL3 to TL4 biota

Food chain multipliers are values derived from relationships of bioaccumulation and biomagnification between trophic levels. These can be determined several ways, depending on the information available. For example, bioaccumulation factors (BAFs) are numeric values showing the amount of contaminant uptake into biota, relative to concentrations in the water column. These BAFs can be determined for each trophic level of aquatic biota. The food chain multiplier for any given trophic level is the ratio of the BAF for that trophic level to the BAF for the trophic level directly below.

For example: BAF for water to trophic level 4 = 680,000
BAF for water to trophic level 3 = 160,000

MTL4 = 680,000/160,000 = 4.25

Any methylmercury concentration estimated for trophic level 3 biota can then multiplied by the MTL4 to estimate the expected concentration in trophic level 4 biota.

If sufficient data on existing fish tissue methylmercury concentrations are available, food chain multipliers can also be established using the ratio of these concentrations between trophic levels.

For example: Average tissue concentration in TL4 fish = 0.45 mg/kg
Average tissue concentration in TL3 fish = 0.15 mg/kg

MTL4 = 0.45/0.15 = 3

For this evaluation, food chain multipliers were calculated from draft national BAFs presented in the EPA's methylmercury criterion document. Although these values are draft only, they were empirically derived from national data. If more site-specific BAF data exist for water bodies in California, they may be used in place of the draft values to calculate food chain multipliers.

Draft national BAF for trophic level 4 = 2,700,000
Draft national BAF for trophic level 3 = 680,000
Draft national BAF for trophic level 2 = 120,000

MTL4 = 2,700,000 / 680,000 = 4
MTL3 = 680,000 / 120,000 = 5.7

Having identified the above input parameters, the following additional terms are necessary to then construct the equation for calculating trophic level concentrations necessary to maintain the overall dietary concentration:

FDTL2 - concentration in food (FD) from trophic level 2
FDTL3 - concentration in food from trophic level 3 - (equivalent to FDTL2 × MTL3)
FDTL4 - concentration in food from trophic level 4 - (equivalent to FDTL2 × MTL3 × MTL4)

The overall dietary concentration (DC) of methylmercury can be expressed in the equation:

$$\mathbf{DC = (\%TL2 \times FDTL2) + (\%TL3 \times FDTL3) + (\%TL4 \times FDTL4)} \quad \mathbf{(1)}$$

The equation can then be further arranged, substituting food chain multiplier equivalents, as:

$$\mathbf{DC = (\%TL2 \times FDTL2) + (\%TL3 \times FDTL2 \times MTL3) + (\%TL4 \times FDTL2 \times MTL3 \times MTL4)} \quad \mathbf{(2)}$$

This equation can then be solved for the concentration in the lowest trophic level:

FDTL2 = DC / [(%TL2) + (%TL3 × MTL3) + (%TL4 × MTL3 × MTL4)] **(3)**

Once the concentration in trophic level 2 is calculated, the remaining trophic levels can be determined using the food chain multiplier relationships:

FDTL3 = FDTL2 × MTL3 **(4)**

FDTL4 = FDTL3 × MTL4 **(5)**

As discussed above, the human health methylmercury criterion document presents a national average intake rate of 17.5 grams of fish per day for the general population. This national average was based on an average consumption of individual trophic levels as follows: TL2 = 3.8 g, TL3 = 8 g, TL4 = 5.7 g. These values correspond to: TL2 = 21.7%, TL3 = 45.7%, TL4 = 32.6%. Using these values, and substituting the TRC for the DC term in Equation 3, the concentration in trophic level 2 biota necessary to maintain the overall dietary concentration can then be calculated.

FDTL2 = TRC / [(%TL2) + (%TL3 × MTL3) + (%TL4 × MTL3 × MTL4)]

FDTL2 = 0.3 mg/kg / [(0.217) + (0.457 × 5.7) + (0.326 × 5.7 × 4)]

FDTL2 = 0.3 / 10.247

FDTL2 = 0.029 mg/kg

Then, using the previously calculated food chain multipliers from above:

FDTL2 = 0.029 mg/kg
FDTL3 = 0.029 × 5.7 = **0.165 mg/kg**
FDTL4 = 0.165 × 4.0 = **0.660 mg/kg**

Based on the trophic level breakout for the default human fish consumption rate identified in the criterion document, the above concentrations of methylmercury will result in an overall dietary concentration (DC) of 0.3 mg/kg:

DC = (%TL2 × FDTL2) + (%TL3 × FDTL3) + (%TL4 × FDTL4)

0.3 mg/kg = (.217 × 0.029 mg/kg) + (.457 × 0.165 mg/kg) + (.326 × 0.66 mg/kg)

II.B. Highest Trophic Level Approach

In contrast to the Average Concentration Trophic Level Approach, the Highest Trophic Level Approach sets the proposed human health methylmercury criterion of 0.3 mg/kg as the limiting concentration in edible portions of trophic level 4 fish. Concentrations expected in trophic levels 2 and 3 can then be estimated using a variation of the food chain multiplier approach described above. In effect, these multipliers determined by the ratios of trophic level concentration relationships become food chain dividers: 0.3 mg/kg in trophic level 4 is divided by the MTL4 to estimate the concentration in trophic level 3, which is then divided by the MTL3 to estimate the concentration in trophic level 2.

FDTL4 = 0.3 mg/kg
FDTL3 = 0.3 / 4 = **0.075 mg/kg**
FDTL2 = 0.075 / 5.7 = **0.013 mg/kg**

This approach is the most conservative (*i.e.*, protective) method of establishing trophic level concentrations with the TRC, as it eliminates the possibility of different human populations exceeding the protective reference dose, assuming the national average consumption rate remains constant. A diet of 100 percent trophic level 4 fish would maintain the overall dietary concentration of 0.3 mg/kg.

III. PROTECTIVE WILDLIFE VALUES

III.A. Selection of Species

The next step in this evaluation was to determine an overall dietary concentration of methylmercury that will protect each species of concern. Species considered in this evaluation include representatives from several taxonomic classes: birds, mammals, fish, reptiles, and amphibians (see Appendix). Initially, the taxonomic class or classes with the greatest potential risk from methylmercury concentrations in fish tissue were identified. For fish species, risk assessment was based solely on adverse effects associated with tissue methylmercury concentrations (see Section X). For non-fish species, the risk assessment was based on exposure through ingestion of methylmercury-contaminated aquatic prey.

The scientific literature contains little information on methylmercury risk to reptiles and amphibians, with no studies found that relate effects to dietary doses (see Section X). Throughout the past several decades, however, a great deal of toxicity research has been conducted on various birds, mammals, and fish. While toxicity data for fish indicate adverse effects resulting from a wide range of tissue methylmercury concentrations, the majority of this research has been conducted with tissue concentrations substantially higher than the TRC. Research on birds and mammals, particularly piscivorous species, is also extensive. Much of this work has involved oral dose studies.

Based on the information available in the scientific literature, and given consideration of methylmercury's capacity to bioaccumulate and biomagnify in the food chain, this evaluation assumed that upper trophic level wildlife species (*i.e.*, predatory birds and mammals) have the greatest inherent risk from exposure to methylmercury, compared to other biota. Wildlife Values (WV), which are the total dietary methylmercury concentrations that will protect predatory birds and mammals, were determined for these upper trophic level species. The methodology then allows for an assessment of whether these values would be exceeded based on the various trophic level concentrations estimated by the two approaches described above. After an analysis of the protection afforded to listed birds and mammals, the scientific literature was reviewed to see whether the listed fish, reptile, and amphibian species may be protected by either trophic level approach.

Listed species for which WVs were generated:

Southern Sea Otter (*Enhydra lutris nereis*)
California Least Tern (*Sterna antillarum brownii*)
California Clapper Rail (*Rallus longirostris obsoletus*)
Light-Footed Clapper Rail (*Rallus longirostris levipe*)
Yuma Clapper Rail (*Rallus longirostris yumaensis*)
Western Snowy Plover (*Charadrius alexandrinus nivosus*)
Bald Eagle (*Haliaeetus leucocephalus*)

III.B. Equation to Calculate Wildlife Values

A Wildlife Value represents the overall dietary concentration of methylmercury necessary to keep the daily ingested amount at or below a sufficiently protective reference dose. Reference doses (RfD) may be defined as the daily exposure to a toxicant at which no adverse effects are expected. In effect, the WV converts the protective RfD into an overall dietary concentration (in mg/kg in diet). The WV is analogous to the TRC for the human health criterion. The WV is calculated using the following equation:

$$\mathbf{WV} = \frac{\mathbf{RfD} \times \mathbf{BW}}{\sum \mathbf{FIR_i}} \qquad \mathbf{(6)}$$

WV = Wildlife Value (mg/kg in diet)
RfD = Reference Dose
BW = Body Weight (in kg) for species of concern
FIR_i = Total Food Ingestion Rate (kg food/day), from the i^{th} trophic level, for species of concern

Because the most sensitive endpoints for toxicity of methylmercury in birds and mammals relate to reproduction, the focus of this methodology is to establish reference doses based on preventing adverse impacts from maternally ingested methylmercury, that could potentially affect the reproductive viability of the species. In order to establish RfDs, the scientific literature was first

reviewed to find the most appropriate toxicity test doses for avian and mammalian species. An uncertainty analysis (described below, Section III.D.) was then conducted for each test dose to arrive at the appropriate RfD. Body weights used in this approach were those of adult females for the species of concern. Total food ingestion rates for species of concem, and the trophic level breakout of the diet, were obtained from the scientific literature or estimated using allometric equations.

III.C. Determination of Test Doses

Once the taxonomic class or classes assumed to be at greatest risk were identified (*i.e.*, predatory birds and mammals), the next step in the evaluation was to identify appropriate toxicity test doses to use for determining a protective RfD for each group. As the species of concern for this evaluation are federally listed as threatened or endangered, the goal of this step was to find the lowest test doses associated with endpoints that could adversely affect the continued existence of the species or the loss of individuals from the population. Most often these toxicity endpoints were based on subtle effects concentrations (*e.g.*, reproductive success), rather than more severe effects in individuals (*e.g.*, lethality). However, if the lowest test dose was found to cause impacts that could effectively remove an individual from the population, even without any apparent effect on reproductive success, this test dose was used in the analyses.

The approach used in this methodology assesses toxicity through ingestion of methylmercury in contaminated prey, so the scientific literature was searched for all available oral test doses demonstrating observable effects concentrations. The data preferences used in this analysis were the same as outlined in the Great Lakes Initiative (GLI) *Technical Support Document for Wildlife Criteria* (U.S. Environmental Protection Agency, 1995c):

- Appropriate endpoints (reproductive or developmental success, organismal viability or growth, other parameters influencing population dynamics)
- Chemical-specific dose-response curve
- Chronic or sub-chronic study duration
- Wildlife species preferred over traditional laboratory animals
- Field studies preferred over laboratory studies
- Oral route of exposure, although other routes acceptable if possible to convert to oral dose

Many oral dose toxicity studies report test doses as the amount of contaminant in the diet of the tested species (*e.g.*, mg/kg food). Therefore, it is often necessary to convert these reported levels to a daily ingested dose (mg/kg-bw/day), using body weights and food ingestion rates for the species studied (*i.e.*, mg/kg in food × kg food consumed per kg body weight per day = mg/kg body weight per day).

For this evaluation, the scientific literature was reviewed with particular emphasis on searching for rigorous data reported since the development of water quality wildlife criteria for the GLI in

1995. For the GLI effort, two studies that best fit the data preferences were selected to calculate the mercury wildlife criteria for avian and mammalian species. These are described below, along with relevant findings from the current literature search.

Mammalian Test Dose: In developing water quality criteria for mercury in the GLI, the EPA reviewed numerous mammalian chronic and subchronic toxicity studies. Test animals studied were rats and mink. Toxicity to mink was evaluated in two subchronic studies by Wobeser *et al.* (1976a,b), and these studies formed the basis for EPA's calculation of the mammalian wildlife criterion for mercury. Each study had different exposure durations (93 and 145 days) and dosing levels. The 145 day study dosed mink with two methylmercury concentrations (0.22 and 0.33 mg/kg) in food. These concentrations corresponded to dietary doses of 0.033 and 0.05 mg/kg-bw/day, respectively, using a food ingestion rate of 0.15 kg/day and a body weight of 1 kg for captive mink. The EPA determined that no adverse effects were seen at either dose, and concluded the 0.05 mg/kg-bw/day constituted a No Observable Adverse Effects Level (NOAEL) test dose.

From the 93 day study, the EPA determined both NOAEL and LOAEL (Lowest Observable Adverse Effects Level) test doses. A concentration of 1.1 mg/kg in food caused pathological alterations in the mink nervous system (nerve tissue lesions), while concentrations of 1.8 mg/kg and higher in food resulted in clinical signs of mercury intoxication [anorexia (loss of appetite) and ataxia (loss of coordination)] and subsequent mortality. Using the same food ingestion rate and body weight converts the 1.1 and 1.8 mg/kg concentrations to dietary doses of 0.16 and 0.27 mg/kg-bw/day, respectively. The EPA concluded that the effects seen in the 0.16 mg/kg-bw/day dose group were not associated with any obvious clinical evidence of toxicity, and that this dose constituted the NOAEL test dose, despite Wobeser's conclusion that distinct clinical signs of toxicity would have resulted had the exposure period been longer. The 0.27 mg/kg-bw/day dose was designated the LOAEL.

For several years, the U.S. Department of Energy (DOE) (1993-1996) has published *Toxicological Benchmarks for Wildlife*. These documents have also used toxicity studies of rats and mink to determine the mammalian benchmarks for methylmercury compounds. In determining final NOAEL and LOAEL values for piscivorous mammals, Wobeser *et al.*'s (1976b) 93 day study was used. The DOE's evaluation of this study agreed with the EPA's conclusion that the 1.1 mg/kg concentration constituted a NOAEL; however, using a slightly different value for the mink food ingestion rate (0.137 kg/day), a dietary dose of 0.15 mg/kg-bw/day was calculated.

In 1997, the EPA published the *Mercury Study Report to Congress* (MSRC). Volume VI of this report (U.S. Environmental Protection Agency, 1997a) presented reviews of several methylmercury toxicity tests with mammalian wildlife, including both Wobeser *et al.* (1976a,b) studies. For the MSRC, the EPA concluded that the nerve tissue lesions observed in the 1.1 mg/kg concentration group from the 93 day study were relevant effects endpoints, noting the researcher's opinion that the nerve tissue damage would have become manifested as impaired

motor function had the study continued for a longer period. For this reason, the EPA assigned the 1.1 mg/kg concentration as the LOAEL. As this was the lowest dosing group in the study, a NOAEL could no longer be determined. Instead, the EPA selected the 0.33 mg/kg concentration from the 145 day study as the NOAEL. Using the food ingestion rate found in the DOE analysis (0.137 kg/day) and a body weight of 0.8 kg (as opposed to 1.0 kg used in both the GLI and DOE reports), the EPA converted the 0.33 mg/kg dose in food to a dietary NOAEL test dose of 0.055 mg/kg-bw/day for the MSRC.

The MSRC also presented findings from a long-term feeding study with domestic cats (Charbonneau *et al*., 1974). Cats were fed various doses of methylmercury, either as methylmercuric chloride in food or as methylmercury-contaminated fish, for two years. The dietary test doses of 0.046 and 0.020 mg/kg-bw/day were determined to be the LOAEL and NOAEL, respectively, based on neurological impairment effects. These values were only used for comparative purposes, however, as the intent of the MSRC effort was to derive water quality criteria that would be protective of wildlife. The NOAEL test dose from the 145 day mink study was used in the subsequent MSRC calculations to derive criteria values for mammalian wildlife.

As all the effects seen in the semi-domesticated mink and domestic cat studies involved toxicity to individual animals, an effort was made for this evaluation to find data on effects to reproductive performance. Wren *et al*. (1987) reported no effects on reproduction in mink fed a diet supplemented with 1.0 mg/kg methylmercury every other day for 150 days. In a two generation study (G1, G2) of mink fed organic mercury-contaminated diets, Dansereau *et al*. (1999) analyzed effects on reproductive performance. Dosing groups were 0.1, 0.5, and 1.0 mg/kg total mercury. Whelping percentage for the G1 females was statistically higher in the 0.1 mg/kg group than in the 0.5 or 1.0 groups. Whelping percentages for all other G1 and G2 dosing groups were low relative to reported performance of untreated female mink. The researchers suggested that the observed linear decrease of performance with increasing methylmercury exposure may have been the result of adverse effects of methylmercury on the reproductive process; however, they were unable to show a statistically significant difference. Although the study could not conclude the reproductive process itself was adversely affected, female mink from both generations in the 1.0 mg/kg suffered mortality from methylmercury intoxication. A large percentage of first generation females died at 11 months of age, after 90 days of exposure. Death occurred approximately one month after whelping the G2 offspring. Second generation females died at the same age as their mothers, but after approximately 330 days of exposure. However, the G2 females had been mated at the age of 10 months and death occurred one month later in 6 out of 7 individuals, before giving birth. The remaining individual died shortly after giving birth. The researchers concluded that "...survival and consequently the reproduction of the G2 females fed 1.0 ppm Hg diet were therefore affected."

Although the 1999 Dansereau *et al*. study could not confirm impaired reproductive performance, it is useful for validating that a concentration of 1.0 mg/kg methylmercury in food represents an observable adverse effects level, which could inhibit the overall success of a population by removing reproductively viable individuals. The researchers found no mortality or neurological

signs of toxicity in any mink in the 0.1 and 0.5 mg/kg diet groups; however, the animals were not sacrificed and examined for histopathological effects in either of these groups. A review of the available scientific literature since the GLI revealed no new data that better fits the GLI preferences or that reports lower oral dose observed effects concentrations for mammalian wildlife. Therefore, the NOAEL dose of 0.33 mg/kg in food (0.055 mg/kg-bw/day) from the 145 day study by Wobeser *et al*. (1976a) is the appropriate test dose for determining protection of piscivorous mammalian wildlife in this evaluation.

Avian Test Dose: For the GLI effort, the EPA also reviewed numerous subchronic and chronic mercury toxicity studies using avian species. Species examined in this review included domestic chicken, pheasant, Japanese quail, red-tailed hawk, zebra finch, and game farm mallard ducks. The EPA ultimately selected a study examining reproductive and behavioral effects in three generations of mallard ducks (Heinz, 1979) to determine an appropriate test dose for its avian wildlife criteria calculations.

In these studies, three generations of mallard ducks were exposed to a mercury-free control diet or one containing 0.5 mg/kg methylmercury dicyandiamide. Several measurements of reproductive success were evaluated throughout the course of the study. Statistically significant adverse effects were observed in the percentage of eggs laid outside the nest box (increase) and in the number of one-week-old ducklings produced (decrease), relative to controls. In addition, adverse behavioral effects were seen in the ducklings from the treatment group, relative to controls. The behavioral aberrations observed included a smaller percentage of ducklings approaching tape-recorded maternal calls, and an increased sensitivity to frightening stimuli, as measured by the distance traveled in avoidance.

Based on the methylmercury concentration tested (0.5 mg/kg in food) and the reported average food consumption rate for 2nd and 3rd generation mallards in the treatment group (0.156 kg/kg-bw/day), the EPA determined a dietary dose of 0.078 mg/kg-bw/day. No lower effects concentration test doses were reported in any of the other avian toxicity studies evaluated by the EPA. As there were no lower treatment concentrations in the mallard studies, the EPA assigned this dietary dose as the LOAEL to be used in avian wildlife value calculations. For the GLI, the EPA (1995b) concluded that the mallard studies best fit the data preferences, providing a chemical-specific dose-response curve and demonstrating effects that "...clearly have potential consequences on populations of mallards exposed to methylmercury."

Although mercury toxicity has been studied extensively using avian species, both before and after the GLI effort, Heinz' (1979) multi-generational mallard work has been used almost exclusively in subsequent efforts to derive water quality values for methylmercury that are protective of avian wildlife (U.S. Department of Energy, 1994-1996; U.S. Environmental Protection Agency, 1997a; Nichols *et al*., 1999; Canadian Council of Ministers of the Environment, 2000; Buchanan *et al*., 2001; California Regional Water Quality Control Board - Central Valley Region, 2001; Evers *et al*., 2002). In large part, this is because few other studies have attempted to establish oral dose-response data from long-term feeding studies. There is a

great deal of scientific literature devoted to methylmercury residues in various avian tissues (*e.g.*, muscle, liver, egg); however, these studies were generally not designed to determine chronic dietary doses. The literature search for this evaluation only revealed a few additional studies, described below, that could be used for evaluating dietary concentrations associated with subchronic or chronic effects.

In a broad survey of freshwater lakes in Canada, which were contaminated with mercury and experienced unnatural water level fluctuations and turbidity, Barr (1986) examined the population dynamics of common loons. Loons in these systems preyed on fish containing various concentrations of methylmercury. Based on his observational data, Barr concluded that adverse reproductive effects in loons (*i.e.*, reductions in egg laying, and nest site and territorial fidelity) were associated with mean fish tissue concentrations ranging from 0.3 - 0.4 mg/kg methylmercury. As this study was not designed as a controlled feeding experiment, Barr did not convert these concentrations into daily ingested doses (*i.e.*, mg/kg-bw/day). However, Barr's reported average body weights for male and female loons (~ 4.0 kg) and assumed food consumption rate of 20 percent body weight per day (0.8 kg/day) allowed for comparison with the 0.078 mg/kg-bw/day dietary dose from the Heinz (1979) mallard work. Multiplying the lowest concentration Barr associated with adverse effects (0.3 mg/kg in fish) and the assumed average food ingestion rate (0.2 kg/kg-bw/day) produces a daily dietary dose of 0.06 mg/kg-bw/day. While the limitations of the Barr study (*i.e.*, no controlled oral dose-response data) prevent the use of this daily value as the appropriate test dose for this evaluation, it serves to support the test dose selected by the EPA for the GLI effort.

Effects of controlled methylmercury dosing on captive great egret nestlings were reported in Bouton *et al*. (1999) and Spalding *et al*. (2000a,b). In these studies, 16 great egret nestlings were captured from the wild and separated into various dosing groups (0, 0.5, 5.0 mg/kg methylmercury chloride in diet) for 14 weeks. Methylmercury was administered via gelatin capsules, and doses were maintained based on daily food consumed. Although dietary concentrations were maintained, the daily amount of methylmercury consumed per kilogram of body weight varied from 0.048 to 0.135 mg/kg-bw/day. This was because nestling body weights and food consumption rates are very dynamic during this intense growth phase. The variation in daily dietary doses limited the usefulness of these studies for determining an appropriate avian test dose for this evaluation; however, analysis of effects observed in the 0.5 mg/kg dose group for each of the three studies (described below) allowed for comparison with the LOAEL concentration from the Heinz (1979) effort.

Bouton *et al*. (1999) measured behavioral effects in the captive egrets during the period of the experiment (10-14 weeks) approximate to post-fledging in wild egrets (11 weeks of age). These researchers concluded that adverse effects, including reduced activity, food intake, and willingness to hunt prey, were demonstrated in the 0.5 mg/kg dosing group. They also postulated that these behavioral effects may result in reduced juvenile survival in free-ranging birds.

Spalding *et al*. (2000a) examined the accumulation of methylmercury in tissues of the captive egrets and its effect on growth and appetite. These researchers hypothesized that nestling wading birds would be less at risk from ingested methylmercury than fledgling birds, due to depuration of the methylmercury into the rapidly growing feathers of the younger birds. Reduced appetite, and a subsequent decline in growth, was observed after the ninth week of the experiment in both the 0.5 and 5.0 mg/kg dose group, corresponding to the cessation of feather growth. Although the magnitude of weight loss was small, the study's authors concluded that the abundance of food in the controlled setting may have masked some of the effects that would have resulted had the birds been hunting on their own. The study results supported the conclusion that, relative to pre-fledging nestlings, post-fledging birds are at an elevated risk from methylmercury exposure at even the 0.5 mg/kg dietary concentration, during the period when feathers stop growing. The researchers noted that this period also coincides with the time that young birds face the multiple risk factors of having to forage on their own, leave the natal colony, and become exposed to novel predation and disease factors.

Spalding *et al*. (2000b) examined the same egrets for histologic, neurologic, and immunologic effects. Both dosing groups exhibited effects of varying magnitude. Birds in the 5.0 mg/kg dose group showed severe ataxia, as well as hematologic, neurologic, and histologic changes, with the most severe lesions in immune and nervous system tissues. The 0.5 mg/kg dosed birds also exhibited multiple effects for various endpoints, relative to birds in the control group. In comparing their findings with effects reported in studies of wild birds, the authors concluded that the thresholds for sublethal effects measured in captive birds were lower than those in wild birds. However, these researchers attributed this discrepancy to the increased detectability of effects in controlled experiments, and suggested that LOAELs from captive studies may be a more accurate predictor of effects for field situations than field-derived LOAELs applied to captive studies.

Taken together, these three studies (Bouton *et al*., 1999 and Spalding *et al*., 2000a,b) demonstrated adverse effects in juvenile piscivorous birds exposed to a diet containing 0.5 mg/kg methylmercury. The multitude of effects reported, while not directly associated with reproduction, could have significant implications for population viability. Even if the number of offspring produced is not affected by a diet containing 0.5 mg/kg methylmercury, the number of juvenile birds becoming breeding individuals may be reduced through impaired fitness or increased mortality. These studies provided validation for adverse effects to avian species resulting from a dietary concentration of 0.5 mg/kg methylmercury.

In a similar evaluation of methylmercury impacts to juvenile piscivorous birds, Henny *et al*. (2002) studied three bird species nesting in a mercury-contaminated watershed. Various tissues and endpoints from both adult and juvenile double-crested cormorants, black-crowned night herons, and snowy egrets were measured, including methylmercury concentrations in stomach contents. Based on stomach content analyses, it was determined that young of these species were fed diets averaging 0.36 - 1.18 mg/kg methylmercury through fledging. Although adult birds were exposed to the same prey pool and had higher total mercury concentrations in their livers than fledglings, the younger birds exhibited greater evidence of sublethal toxicity to their

immune, detoxification, and nervous systems. The strongest evidence of these effects was seen in the cormorants, which had the highest average methylmercury concentration reported from stomach content analysis (1.18 mg/kg). However, these effects were also observed in the other species, with average dietary concentrations of 0.36 mg/kg (snowy egrets) and 0.43 mg/kg (black-crowned night herons). No conclusions could be drawn regarding post-fledging survival, as the study concluded at about the time of fledging. However, noting that many of the fledglings remained in the watershed after leaving the nest area, the study authors suggested that the additional period of foraging in the contaminated system, coupled with the completion of feather growth, may have critically increased the body burden of mercury and its potential toxicity.

None of the studies described above (Barr, 1986; Bouton *et al*., 1999; Spalding *et al*., 2000a,b; Henny *et al*., 2002) provided a suitable avian oral test dose for methylmercury that could be used as an alternative to the one generated in the Heinz (1979) work with mallard ducks. They do, however, confirm that a concentration of methylmercury in food around 0.5 mg/kg is sufficient to cause significant adverse effects to avian reproduction and health that could have deleterious impacts at both the individual and population levels. A review of the scientific literature revealed no other dose-response studies that established appropriate oral test doses for avian species, and the Heinz (1979) work remains the most robust benchmark for evaluating impacts to birds from methylmercury in the diet.

The body of work on mercury toxicity to avian species includes a great deal of data on residue concentrations in various tissues (*e.g.*, brain, liver, feather). Often these studies have attempted to establish threshold concentrations in specific tissues correlated with adverse effects. The use of egg concentrations is often cited as a valuable endpoint in evaluating the toxicity of methylmercury, as developing embryos are more sensitive than adults (Wiener *et al*., 2002). Reviews of studies reporting data on mercury concentrations in eggs of both wild and captive birds can be found in Thompson (1996), Burger and Gochfeld (1997), Wolfe *et al*. (1998), and Eisler (2000). However, as important as these studies are for determining concentrations associated with embryotoxic effects, relatively few provide information on the dietary doses of the laying birds that resulted in the observed egg methylmercury concentrations.

The two most commonly cited studies reporting egg methylmercury concentrations and adverse effects resulting from controlled feeding studies examined pheasants (Fimreite, 1971) and mallards (Heinz, 1979). The mallard study is the same as the one discussed above, used in determining the LOAEL dietary test dose for the GLI. From a dietary concentration of 0.5 mg/kg methylmercury, Heinz (1979) reported an average concentration over three generations of 0.83 mg/kg wet weight in eggs. Although mallard embryos were not examined for signs of toxicosis, the egg concentrations reported resulted from a dietary dose causing adverse reproductive effects. Fimreite's (1971) controlled dosing experiment with ring-necked pheasants demonstrated reduced hatchability, expressed as the percentage of eggs incubated, in egg samples containing between 0.5 - 1.5 mg/kg methylmercury. This range is similar in magnitude to the average egg concentration (0.83 mg/kg) reported by Heinz (1979), and the lower end (0.5 mg/kg) is often

cited as a LOAEL for avian eggs (Wolfe *et al.*, 1998). Based on the egg concentrations and associated adverse reproductive effects reported in these two studies, it is generally accepted in the scientific literature that eggs of pheasants are more sensitive to methylmercury than mallard eggs. However, the dietary concentrations (~ 2-5 mg/kg) resulting in the range of egg concentrations observed in pheasants by Fimreite (1971) were substantially higher than the 0.5 mg/kg dietary concentration causing the similar egg values reported in mallards by Heinz (1979). This indicates a substantial difference between these species in the transfer efficiency from methylmercury in the maternal diet to methylmercury in the egg.

Recent and ongoing efforts by Heinz (pers. comm., 2003) are focused on more closely examining interspecies differences in sensitivity to egg methylmercury concentrations. Through direct injection into the eggs of various bird species, different concentrations of methylmercury can be evaluated as to their effects on developing embryos. Preliminary results seem to confirm the findings from the feeding studies described above that pheasant eggs are more sensitive than mallard eggs. In addition, there appears to be a broad range of species sensitivity, both more and less sensitive than mallard eggs. While the data from these efforts, when published, will provide important information concerning the relative magnitude of sensitivity exhibited by different species, their utility for evaluating effects from dietary methylmercury is limited by two constraints. First, it requires less methylmercury to cause adverse effects in eggs when it is injected than when naturally deposited by the mother. Therefore, species-specific LOAELs for eggs cannot be determined from injected concentrations until a relationship to maternally-deposited concentrations can be accurately determined. Second, as seen with the pheasant and mallard feeding studies, there may be wide variations among species in diet-to-egg transfer efficiency. Selecting an egg LOAEL based on the most sensitive species examined in injection studies may correspond to a higher dietary concentration, relative to other species with higher egg LOAELs.

As no other toxicity data were found that could provide a more appropriate oral test dose for avian species, the results of the Heinz (1979) study with mallard ducks was used for this evaluation. However, discrepancies were noted in the scientific literature regarding how these results were used to convert the dietary concentration (mg/kg in food) to a daily dose (mg/kg-bw/day). As described above, the EPA used the average food consumption rate for 2nd and 3rd generation mallards in the treatment group (0.156 kg/kg-bw/day) to calculate a dietary dose of 0.078 mg/kg-bw/day for use in the GLI avian wildlife criterion derivation (U.S. Environmental Protection Agency, 1995d). In a departure from this approach, the U.S. Department of Energy (1993-1996) used the average food consumption rate for the study's control group (0.126 kg/kg-bw/day) to calculate a dietary dose of 0.064 mg/kg-bw/day for the derivation of toxicological benchmarks for wildlife. This lower value has been used in Wolfe and Norman (1998) and California Regional Water Quality Control Board - Central Valley Region (2001), while the higher value has been used in Nichols *et al.* (1999), Canadian Council of Ministers of the Environment (2000), Buchanan *et al.* (2001), and Evers *et al.* (2002). Further confounding the matter, the MSRC used the higher value in one volume (Vol. VI) (U.S. Environmental Protection Agency, 1997a) and the lower value in a different volume (Vol. VII) (U.S. Environmental

Protection Agency, 1997b), although the higher value was used in the Report to calculate water quality criteria.

In an effort to understand the rationale for using the control group's food consumption rate to calculate a LOAEL, the author of the 1979 mallard study was contacted (Heinz, pers. comm., 2002). Heinz stated that the difference in his reported ingestion rates for the two study groups was not due to greater wastage on the part of the treatment group, and further, that the reported rates were probably not very accurate for either group. He explained that the ability to distinguish wasted food from the debris at the bottom of test subject cages (fecal matter, undigested food, *etc*.) was insufficient to calculate feeding rates with a great degree of precision. However, based on his understanding of work subsequent to the 1979 study, Heinz believes that true mallard feeding rates are likely even lower than the rates he reported (0.1 kg/kg-bw/day vs. 0.128 and 0.156). While Heinz did not suggest a 0.1 kg/kg-bw/day ingestion rate be used to determine the LOAEL, he did caution against using the 0.156 kg/kg-bw/day rate reported for his 1979 treatment group. This conversation supported the use of the 0.064 mg/kg-bw/day LOAEL calculated with Heinz' control group feeding rate as the appropriate dietary dose for evaluating risk to avian species, with the acknowledgment that true mallard feeding rates may suggest the need for a lower LOAEL.

III.D. Determination of Reference Doses

As noted previously, a reference dose (RfD) may be defined as the daily exposure to a toxicant at which no adverse effects are expected, analogous to NOAEL doses determined from toxicity tests. However, RfDs are intended to protect all species likely to be at risk from exposure to the contaminant, from each taxonomic class for which test doses were determined. Ideally, toxicity tests to determine chronic effects of a contaminant will be of sufficient duration and dose spacing to allow for establishment of a reliable NOAEL. For a variety of reasons, the duration and dose spacing of many toxicity tests are not suitable for this, and NOAELs must be extrapolated from the test information available. In addition, any NOAELs established may only be applicable for the species tested. Extrapolating any given test dose into a RfD at which no adverse effects are expected, for potentially a broad range of species, involves some amount of uncertainty.

In order to determine the RfD for a given taxonomic group, the test dose selected to represent that group may need to be adjusted by uncertainty factors to incorporate variability in toxicological sensitivity among species and to extrapolate for duration (subchronic-to-chronic) or dose spacing (LOAEL-to-NOAEL) issues. The RfD is calculated using the following equation:

$$\mathbf{RfD} = \frac{\mathbf{TD}}{\mathbf{UF_A} \times \mathbf{UF_S} \times \mathbf{UF_L}} \qquad \mathbf{(7)}$$

RfD = Reference Dose (mg/kg-bw/day)
TD = Test Dose (mg/kg-bw/day)
UF_A = Interspecies Uncertainty Factor (unitless)
UF_S = Subchronic-to-Chronic Uncertainty Factor (unitless)
UF_L = LOAEL-to-NOAEL Uncertainty Factor (unitless)

The concept of adjusting test doses to account for these types of uncertainty has been widely used in efforts to develop avian and mammalian reference doses for methylmercury that would be protective of a range of wildlife species (U.S. Department of Energy, 1993-1996; Canadian Council of Ministers of the Environment, 2000; Buchanan *et al*., 2001; California Regional Water Quality Control Board - Central Valley Region, 2001; Evers *et al*., 2002). However, the majority of these efforts have used the same uncertainty factors originally determined in either the GLI effort (U.S. Environmental Protection Agency, 1995d) or the MSRC (U.S. Environmental Protection Agency, 1997a,b). Guidance on determining the appropriate values for each uncertainty factor can be found in two EPA documents: *Technical Basis for Recommended Ranges of Uncertainty Factors used in Deriving Wildlife Criteria for the Great Lakes Water Quality Initiative* (Draft Report) (Abt Associates Inc.,1995) and Great Lakes Water Quality Initiative *Technical Support Document for Wildlife Criteria* (U.S. Environmental Protection Agency,1995a).

Mammalian RfD: As described previously in Section IV,C (Determination of Test Doses), the EPA selected studies by Wobeser *et al*. (1976a,b), in both the GLI and the MSRC, to determine the appropriate mammalian test dose for calculating the RfD. However, the two efforts applied different assumptions and arrived at different test doses. For the GLI, a test dose of 0.16 mg/kg-bw/day was determined to be the NOAEL, while the MSRC concluded the test dose of 0.055 mg/kg-bw/day was the appropriate NOAEL. In addition to this difference, each effort then applied different uncertainty factors to each test dose to determine the RfD.

In the GLI, the UF_A and UF_L were both assigned a value of 1. This was because the experimental animal (mink) and the representative species to be protected (river otter) are closely related and assumed to be similarly sensitive, and because the study identified a NOAEL. The UF_S was set at a value of 10 because the study chosen (Wobeser *et al*., 1976b) was of subchronic duration. Applying these three combined uncertainty factors to the test dose of 0.16 mg/kg-bw/day resulted in a mammalian RfD of 0.016 mg/kg-bw/day.

For the MSRC, the UF_A and UF_L were also both assigned a value of 1, for the same reasons outlined above. However, the UF_S for this effort was set at a value of 3 because the effects observed at the subchronic NOAEL (Wobeser *et al*., 1976a) were not associated with overt signs of toxicity (Nichols *et al*., 1999). Applying these three uncertainty factors to the test dose of 0.055 mg/kg-bw/day resulted in a mammalian RfD of 0.018 mg/kg-bw/day.

So despite the discrepancy regarding the appropriate test dose for mammals, both efforts arrived at roughly the same mammalian RfD. The single mammalian species of concern for this

evaluation is the southern sea otter (*Enhydra lutris nereis*), in the same taxonomic family (*Mustelidae*) as the mink and river otter. Therefore, no further adjustments to the UF_A or UF_L were necessary. The analyses regarding the mammalian test dose and UF_S presented in the MSRC represent the most current comprehensive assessment of these Wobeser *et al*. (1976a,b) studies. As a result, **a mammalian RfD of 0.018 mg/kg-bw/day** was used in this evaluation (Table 1.).

Avian RfD: Similar discrepancies concerning uncertainty factors for the avian RfD were noted between the GLI and the MSRC. Both of these efforts agreed on an avian test dose (0.078 mg/kg-bw/day) from the three generation mallard duck study (Heinz, 1979), and both agreed that the UF_S should be assigned a value of 1 because the study was of sufficient chronic duration. However, varying assumptions regarding LOAEL-to-NOAEL relationships and interspecies sensitivity resulted in each effort assigning different UF_L and UF_A values.

Regarding the UF_L, a value of 2 was assigned for the GLI because the LOAEL identified by the EPA from the mallard study, 0.078 mg/kg-bw/day, "...appeared to be very near the threshold for effects of mercury on mallards." As explained in Nichols *et al*. (1999), a range of 1 - 10 was used to set the UF_L values in the GLI, based on an evaluation of chronic toxicity studies with wildlife species using five chemicals (cadmium, DDT, DDE, dieldrin, and mercury). This conclusion was reached after determining that 97 percent of the LOAEL-to-NOAEL ratios examined were less than or equal to 10 and 50 percent were less than or equal to 3.

In contrast, the authors of the MSRC evaluated toxicity studies with methylmercury only. Twenty LOAEL-to-NOAEL ratios were calculated, with the majority between 1 - 2 or 4 - 5 (Nichols *et al*., 1999). For the final calculations of wildlife criteria values in the MSRC, the UF_L was assigned a value of 3. The MSRC (Vol. VI) concluded that "Given the substantial uncertainties in all the values used to calculate the WC for mercury exposure, neither two nor three can be considered to be the only correct value" (U.S. Environmental Protection Agency, 1997a).

The conceptual basis for use of a UF_A is that toxicokinetic and/or toxicodynamic differences among species may result in variable responses to the same applied dose. Empirical data from acute and chronic toxicity tests with wildlife species support the use of a UF_A ranging from 1 to 100 when extrapolating toxicological effects across species. Values tending toward the lower end of this range may be justified by several factors including: 1) the amount and quality of available testing data, 2) a close taxonomic relationship between the tested species and the species of interest, 3) similarity in size of the tested species and the species of interest, and 4) toxicokinetic and / or toxicodynamic information which would suggest that the tested species is likely to be more sensitive than the species of interest.

For the GLI, a UF_A greater than 1 was recommended because of the need to extrapolate mallard data to species in different taxonomic orders, and because of the possibility that another of the species (pheasant) examined in toxicity studies might prove more sensitive if given a longer

exposure duration. However, because the analysis of suitable avian toxicity values reviewed for the GLI indicated that the mallard was possibly the most sensitive to mercury of the six species examined, the conclusion was drawn that a UF_A of 10 would likely be overly conservative. A UF_A of 3 (half-way between 1 and 10 on a log 10 scale) was therefore applied as a reasonable protection for those species that may be more sensitive than mallards.

The question of interspecies sensitivity was revisited in the MSRC. The three species selected in the GLI to represent avian wildlife (belted kingfisher, herring gull, bald eagle) are piscivorous birds. The authors of the MSRC cited literature suggesting that piscivorous birds possess, in comparison to non-piscivorous birds, a greater capacity to demethylate and thereby detoxify methylmercury. Although piscivorous birds are likely faced with the greatest exposure to methylmercury, the MSRC authors concluded that these birds are unlikely to be more sensitive than mallard ducks (an omnivorous species) to the toxic effects of methylmercury, and that application of a UF_A greater than 1 was unwarranted for piscivorous species. Research conducted since publication of the MSRC has provided additional support for the existence of a protective demethylating capability in piscivorous birds (Henny *et al*., 2002). As the species selected in the MSRC to represent avian wildlife (belted kingfisher, loon, osprey, bald eagle) are also piscivorous, the UF_A for that effort was assigned a value of 1. In summary, the uncertainty factors used in both the GLI and the MSRC to adjust the mallard test dose to an avian RfD were as follows:

	GLI	MSRC
UF_A	3	1
UF_S	1	1
UF_L	2	3

For this evaluation, two of the federally-listed avian species of concern are primarily (bald eagle) or exclusively (California least tern) piscivorous. For these species, the rationale used in the MSRC to assign a UF_A of 1 is therefore applicable. This effort differs, however, from both the GLI and MSRC efforts insofar as it includes consideration of four species (California clapper rail, light-footed clapper rail, Yuma clapper rail, and snowy plover) which feed extensively on invertebrates, including (in the case of the snowy plover) invertebrates of non-aquatic origins.

No information could be found regarding the capability of clapper rails or snowy plovers to detoxify methylmercury. Henny *et al*. (2002) provided some data indicating that adult birds whose diet consists largely of aquatic invertebrates may also possess this detoxifying capacity. In this study, Henny *et al*. examined three bird species nesting in a mercury-contaminated watershed. Examination of stomach contents for two of these species, black-crowned night herons (*Nycticorax nycticorax*) and snowy egrets (*Egretta thula*), revealed diets ranging from 100 percent fish to 100 percent large aquatic insect larvae. The diet of the third species, double-crested cormorant (*Phalacrocorax auritus*), was comprised entirely of fish. Analysis of livers from all three species indicated that hepatic demethylation, possibly in a dose-dependent

relationship, allowed adult birds to tolerate relatively high mercury concentrations without apparent adverse effects. Fledglings did not exhibit the same degree of tolerance to liver mercury concentrations; however, the study ended before it could be determined whether hepatic demethylation would become more pronounced as the fledglings matured. The results of this study lend support to the idea that even birds that are not strictly piscivorous, but still primarily consume aquatic biota, may be less sensitive to methylmercury than the non-piscivorous mallard.

However, as described previously in the section on avian test doses, there has been recent work on interspecies sensitivity to methylmercury using egg injection studies (Heinz, pers. comm., 2003). The clapper rail is one of the species examined thus far whose sensitivity to methylmercury in the egg appears to be greater than the mallard, perhaps closer in sensitivity to the pheasant. These results are preliminary only, and presently it is impossible to translate differences in sensitivity of clapper rail and mallard duck eggs to an injected dose of methylmercury into an ecologically meaningful comparison. No information was available from this work on the amount of methylmercury in food necessary to achieve any observed egg effects concentrations or on the relationship of observed effects concentrations to a maternally-deposited dose. The diet-to-egg transfer efficiency can vary widely between different species, as evidenced by the controlled feeding studies with mallards (Heinz, 1979) and pheasants (Fimreite, 1971). It would be imprudent to assume that similar sensitivities to egg concentrations between the clapper rail and the pheasant would necessarily be caused by the same dietary concentration. However, although no definitive conclusions can presently be drawn as to whether the clapper rail is more or less sensitive to methylmercury in food than the mallard, the need for a greater UF_A for this species in determining a reference dose could not be ruled out.

Based on the information outlined above, the uncertainty factors presented in the MSRC are more generally appropriate than those from the GLI for determining the avian reference dose. However, because several of the bird species considered in this effort are not obligate piscivores, the argument presented in the MSRC for using a UF_A of 1 may not be appropriate for these species. For this reason the derivation and subsequent assessment of WVs was based on a UF_A of 1 for piscivorous avian species (least tern and bald eagle) and UF_As of both 1 and 3 for the snowy plover and clapper rails. The UF_A of 3 was selected using the same rationale from the GLI (*i.e.*, half-way between 1 and 10 on a log scale). The alternative reference doses generated by the two UF_As provided for a comparative analysis of protection afforded by both evaluation approaches.

Based on the avian TD of 0.064 mg/kg-bw/day from the Heinz (1979) mallard duck study, and the uncertainty factors from the MSRC, **an avian RfD of 0.021 mg/kg-bw/day** was used in this evaluation (Table 1.). An **alternative avian RfD of 0.007 mg/kg-bw/day** was also presented for the three clapper rail subspecies and the snowy plover.

Table 1. Test Doses, Uncertainty Factors, and Reference Doses for Birds and Mammals

	Mammals	All Birds	Clapper Rails / Snowy Plover
Test Dose	0.055 mg/kg-bw/day	0.064 mg/kg-bw/day	0.064 mg/kg-bw/day
UF_A	1	1	3
UF_S	3	1	1
UF_L	1	3	3
RfD	0.018 mg/kg-bw/day	0.021 mg/kg-bw/day	0.007 mg/kg-bw/day

IV. CALCULATING WILDLIFE VALUES: BODY WEIGHTS, DIETARY COMPOSITION, FOOD INGESTION RATES

Once the RfDs for each taxonomic group were determined from the appropriate test doses, species-specific WVs were calculated (Equation 6; see page 7). This required information on average adult female body weights (kg) and species-specific daily food ingestion rates (FIR *in* kg food/day). References for body weights are provided in each species account below.

Allometric calculations to determine FIRs for numerous wildlife species have been developed by Nagy (1987 and 2001), based on measurements of free-living metabolic rates (FMR) and the metabolizable energy (ME) in various foods (*e.g.*, fish, birds, mammals). Generic allometric equations from Nagy (1987) to calculate FIRs for broad categories (*e.g.*, all birds, passerines, seabirds) were presented in the *Wildlife Exposure Factors Handbook* (U.S. Environmental Protection Agency, 1993). These equations provide FIR in grams of dry matter per day, which can then be converted to wet weight based on percent moisture in the food. More recent work by Nagy (2001) expanded on the development of generic allometric equations, providing both dry weight and wet weight calculations for a broader range of distinct wildlife categories (*e.g.*, Charadriiformes, Galliformes, Insectivorous Birds, Carnivorous Birds). However, because all the generic allometric equations are based on the compilation of metabolic data from a wide range of species, they may not provide the most accurate estimate of FIRs for specific species of concern. If available, estimates of FMR, dietary composition, and assimilation efficiency (AE) for the species of concern should be considered, as this information will provide a more accurate estimate of daily food requirements.

Dietary composition, the amount of each food type consumed on a daily basis, is a critical component in determining FIR, as different foods provide different amounts of gross energy (*e.g.*, kcal/g food matter) to the consumer. For example, the gross energy (GE) available from aquatic invertebrates is greater than that available from aquatic algae (U.S. Environmental

Protection Agency, 1993). The AE values for different foods may also vary substantially. For example, a bird eating aquatic invertebrates assimilates the available energy at a substantially higher efficiency (77%) than if it were eating aquatic vegetation (23%) (U.S. Environmental Protection Agency, 1993). Therefore, the amount of aquatic invertebrate food necessary to fulfill the energetic requirements of a bird consumer would be substantially less than the amount of aquatic vegetation needed to meet the same requirements.

In addition to providing the percentages of each food type in a wildlife consumer's diet, feeding ecology studies can establish the trophic level composition of the diet. While this information is not necessary for calculating WVs, it is essential for evaluating whether either of the TRC trophic level approaches presented here will result in an exceedance of the WVs. Ideally, dietary information on both food type amounts and trophic level composition can be determined in percent biomass, as this provides the most accurate representation of actual ingestion. However, due to the difficulty inherent in determining the exact daily dietary composition of any free-living animal, dietary studies often rely on frequency of feeding observations or analysis of prey remains or a combination of both. These types of data pose less of a problem if the prey species are the same kind (*e.g.*, all fish) and roughly the same size. As the diversity of the prey base increases, however, the relative contribution from each prey item to the daily ingested biomass can be over- or under-represented if reported on the basis of occurrence frequency. For example, observations of predation may indicate an animal consumes small crabs and clams in equal amounts (*i.e.*, 50% clams:50% crabs). However, clams may provide more biomass per animal consumed than crabs, indicating the need for a different dietary ratio (*e.g.*, 70% clams:30% crabs) in estimating food ingestion rates and determining whether WVs will be exceeded.

The following accounts present the best available information regarding dietary composition and FIRs for the species of concern in this evaluation. When species-specific information regarding metabolic needs and assimilation efficiencies for various food types was not available, FIRs were determined using the most appropriate allometric equations from Nagy (2001). When this information was available, FIRs were determined using equations to estimate FMR (Nagy, 1987) and the methodology described in the *Wildlife Exposure Factors Handbook* (U.S. Environmental Protection Agency, 1993). The reader is directed to the three references mentioned for a complete explanation of the allometric methodology.

As the goal of the evaluation was to consider potential effects to animals living and breeding in California, every attempt was made to find the most rigorous dietary data for resident animals. For some species, few detailed feeding studies have been conducted. As a result, some of the following dietary information is based on only one or two studies, some conducted several decades ago. Until new data are generated, however, these studies remain the best source for dietary information.

IV.A. Southern Sea Otter (*Enhydra lutris nereis*):

Sea otters are the largest member of the Mustelidae family but one of the smallest marine mammals (Riedman and Estes, 1988). Based on length measurements of dead sea otters in California, the predicted average weights of healthy animals are 29.0 kg (males) and 19.8 kg (females) (Riedman and Estes, 1990). Although individual body weights may vary from these values, the predicted **average weight for female otters (19.8 kg)** was used for the calculation of wildlife values in this evaluation.

Information on southern sea otter diet was taken primarily from Riedman and Estes (1988, 1990). The diet of southern sea otters rarely or never includes fish, instead being comprised almost exclusively of benthic macroinvertebrates. Over 60 different invertebrate species have been identified as prey items of southern sea otters. However, sea otter diet is influenced by prey species availability, length of time otters have occupied an area, habitat type, and time of year.

Southern sea otters are primarily associated with subtidal habitats characterized by rocky substrata, although they are also found in areas with soft-sediment substrata. The main prey items in rocky subtidal habitats are abalones (*Haliotis* spp.), rock crabs (*Cancer* spp.), and red sea urchins (*Strongylocentrotus* spp.) (Riedman and Estes, 1988). Abalones and sea urchins are predominantly herbivorous, while rock crabs (*e.g.*, red crab, Dungeness crab) are carnivorous on small crustaceans, clams, and oysters (Morris *et al.*, 1980). Sea otters in soft-sediment substrata also rely heavily on bivalve molluscs (*e.g.*, Pismo, Washington, and gaper clams), although the 13 soft-sediment species identified as prey in these habitats include rock crabs and the Lewis's moon snail (*Polinices lewisii*) (Kvitek and Oliver, 1988). The moon snail is primarily a predator on clams (Morris *et al.*, 1980).

In addition to the aforementioned invertebrates, southern sea otter diets can include a wide variety of prey: kelp crabs (*Pugettia* spp.), turban snails, mussels (*Mytilus* spp.), octopus (*Octopus* spp.), barnacles (*Balanus* spp.), scallops (*Hinnites* spp.), fat innkeeper worms, sea stars (*Pisaster* spp.), and chitons (*Cryptochiton* spp.) (Riedman and Estes, 1990). Seasonal abundance can also play a role in determining important food items. Squid, spawning during fall and spring in Monterey Bay, constitute a large component of some sea otter diets (Riedman and Estes, 1990). Sea otters also occasionally prey on various seabirds, including western grebes (*Aechmophorous occidentalis*), surf scoters (*Melanitta perspicillata*), cormorants (*Phalacrocorax* spp.), common loons (*Gavia immer*), and gulls (*Larus* spp.). However, observations of this foraging behavior suggest that it is rare and that male otters may be responsible for the majority of seabird predation (Riedman and Estes, 1990).

The diet of southern sea otters may include a number of species considered trophic level 3 organisms (*e.g.*, octopus, squid, rock crab, moon snail, sea stars), although trophic level 2 organisms (*e.g.*, abalones, clams, mussels, urchins) appear to be the predominant prey. However, diet and foraging strategy appear to vary between individual otters, even within the same foraging habitat (Riedman and Estes, 1988). Sea otters appear to specialize on certain available

prey species, and these preferences may be maintained for several years. Observations of tagged female sea otters in Monterey Bay provided examples of this specialization, with one female preferentially eating kelp crabs, turban snails, and purple urchins, while another female foraged on abalones and rock crabs (Riedman and Estes, 1988).

This apparent foraging specialization, coupled with the diverse array of prey known to be consumed by sea otters, makes it difficult to assign a particular dietary trophic level composition. In a study of foraging in soft-sediment habitats, clams (trophic level 2) were captured and eaten on more than 75 percent of successful foraging dives (Kvitek and Oliver, 1988). Crabs considered trophic level 3 organisms (*Cancer* spp.) appeared to account for only a small percentage (~ 4%) of the diet, with other, lower trophic level crabs (*e.g.*, mole crab, kelp crab) and molluscs comprising the remainder. No comparable estimations of dietary composition were found for otters in rocky habitats, although it appears generally accepted that trophic level 2 organisms like abalones and sea urchins account for the majority of food consumed by these otters. However, based on the availability of a variety of trophic level 3 prey and the potential for individual otters to specialize on certain species, the dietary composition used for evaluating the TRC trophic level approaches for sea otters was **20 percent trophic level 3, 80 percent trophic level 2**. These are not static values and further research may indicate the need for an alternate estimation of dietary composition.

It has been estimated that free-ranging adult sea otters may consume food equivalent to 23-33 percent of their body weights per day (Riedman and Estes, 1990). Using the high end of this range (*i.e.*, 33%) as a conservative approach to represent the assumed higher metabolic needs of a breeding female sea otter, and the predicted average female weight of 19.8 kg results in a daily food ingestion rate of 6.5 kg/day. This estimate of FIR is substantially higher than what would be expected using any of the allometric equations described previously. However, this apparent discrepancy may be explained by considering the sea otter's metabolism and energetic requirements. Sea otters are small relative to other marine mammals, and lack the blubber layer which provides insulation and an energy reserve. Sea otters compensate for the thermal stress of a marine existence by maintaining a high level of internal heat production; 2.4 - 3.2 times that expected for a terrestrial mammal of similar size (Riedman and Estes, 1990). Based on the otter's elevated energetic requirements, it has been estimated that a 20 kg adult would need between 4,295 and 5,750 kcal/day (Riedman and Estes, 1990), roughly twice the FMR estimated using Nagy's allometric equation for all placental mammals (U.S. Environmental Protection Agency, 1993).

FIR for southern sea otter = 6.5 kg wet weight/day

IV.B. California Least Tern (*Sterna antillarum browni*):

The least tern is the smallest of the tern species that nest on open beaches and islands free of vegetation (Thompson *et al*., 1997). Adult female body weights presented in this reference range from 36 - 62 g; however, this range includes three geographic subspecies: *S. a. antillarum* (U.S.

Atlantic/Gulf coasts, West Indies); *S. a. athalassos* (interior U.S.); and *S. a. browni* (California coast, west coast of Mexico). The mean weight for *S. a. antillarum* is 49.3 g, while that of *S. a. athalassos* is 42.5 g. The reported weight for *S. a. browni* (39.8 g) was only based on one specimen. Dunning (1993) reported a mean weight of 43.1 g (unknown sex) for breeding birds in Kansas (most likely *S. a. athalassos*). Using the mean weights reported in Thompson *et al.* (1997) for the two coastal subspecies results in an **average adult female body weight of 45 g**.

Although other subspecies' diets include small crustaceans and insects (Thompson *et al.*, 1997), the California least tern appears to be strictly piscivorous (Massey, 1974). Breeding colonies may form on beach sites along the coast or on suitable alternative substrates set back from the ocean (U.S. Fish and Wildlife Service, 1985a). Colonies are generally located either near the coast, or near lagoons, estuaries, or rivers (Thompson *et al.*, 1997).

Individuals from three breeding colonies near the coast, that had little or no freshwater or estuarine habitats nearby, were found to forage almost exclusively in relatively shallow, nearshore ocean waters in the vicinity of major river mouths (Atwood and Minsky, 1983). Terns were observed to feed on three primary forage fish species: northern anchovy (*Engraulis mordax*) and two species in the silversides family - topsmelt (*Atherinops affinis*) and jacksmelt (*Atherinopsis californiensis*). Prey size at two coastal colonies varied for each tern age class, with chicks consuming smaller fish than adults or juveniles. However, 73 percent of the three primary forage fish species eaten by all age classes were less than 5 cm in length (Atwood and Kelly, 1984).

In contrast to tern colonies which foraged mainly in nearshore ocean waters, terns from breeding colonies located near estuarine habitats fed primarily in shallow saltmarsh channels and tidal estuaries (Atwood and Minsky, 1983; Atwood and Kelly, 1984). The dominant forage fish species in these waters, and the majority (82%) of fish dropped at a colony in Anaheim Bay, were the topsmelt and California killifish (*Fundulus parvipinnis*). Atwood and Kelly (1984) found that fish dropped at breeding tern colonies, either accidentally or from lack of hunger, were generally valid indicators of the principal prey species consumed. Two other forage fish, deepbody anchovies (*Anchoa compressa*) and slough anchovies (*Anchoa delicatissima*), were the most abundant prey dropped at two southerly colonies, although no distinction was made as to where terns from these colonies foraged (Atwood and Kelly, 1984). Although a total of 49 forage fish species, all represented by individuals less than 1 year old, were found at 10 breeding tern colonies, Atwood and Kelly (1984) concluded that five fish (northern anchovy, topsmelt, jacksmelt, deepbody anchovy, slough anchovy) represented the main food items at least tern breeding colonies in California.

Foraging ecology for a tern breeding colony located near San Francisco Bay has been monitored for numerous years, providing a long-term assessment of the colony's dietary preferences (Elliott and Sydeman, 2002). Prey fish dropped at the colony by foraging birds were collected and identified from 1981-1982, 1984-1995, and 2000-2001. Although minor variations in forage fish species abundance were reported between years, the combined data from all years revealed that

three fish (topsmelt, jacksmelt, northern anchovy) accounted for more than 86 percent of all samples collected. The next most abundant prey (> 7% of total) were various surfperch species (*Embiotocidae*).

Based on the above information, the diet of adult female California least terns is comprised solely of small fish from various species. Several of these species (northern anchovy, topsmelt, jacksmelt, Califomia killifish) appear to account for the majority of prey items taken by both courting and nesting terns, including those birds that forage in estuarine and tidal waters. In addition, data indicate that the majority of fish captured by breeding terns are small (5 cm or less) and all are young-of-year (Atwood and Kelly, 1984). According to the *Trophic Level and Exposure Analyses for Selected Piscivorous Birds and Mammals* (Vol. III) (U.S. Environmental Protection Agency, 1995b), these prey species are generally considered trophic level 3. Even juvenile fishes from this group (*e.g.*, topsmelt, northern anchovy) are listed as trophic level 3 by this reference.

It is important to note that all of these forage fish species exhibit some amount of omnivory, feeding to varying degrees on primary producers and detritus. Juvenile northern anchovies generally consume small crustaceans and other zooplankton, although algae and other phytoplankton may constitute a substantial portion of their diet (Wang,1986). Anchovies can be filter-feeding or biting planktivores, indicating the ability to selectively prey on individual organisms (California Department of Fish and Game, 2001). Similarly, the diet of the California killifish consists primarily of benthic and planktonic invertebrates, with juveniles more likely than adults to feed on terrestrial insects and zooplankton (Moyle, 2002). West and Zedler (2000) examined gut contents of adult killifish and reported algae and detritus as minor dietary items. Nonetheless, both anchovy and killifish appear to feed primarily on trophic level 2 organisms.

In contrast to the anchovy and killifish, the feeding habits of the other two primary tern prey fish (topsmelt and jacksmelt) indicate a greater dietary dependence on trophic level 1 food. Wang (1986) listed the major food items for juvenile jacksmelt as algae, detritus, and small crustaceans. In addition, amphipods were described as a common food item. The same reference (Wang, 1986) states that juvenile topsmelt feed on crustaceans, diatoms, algae, detritus, chironomids, and amphipods. The California Department of Fish and Game (2001) states that topsmelt inhabiting intertidal areas consume algae and fly larvae, as well as crustaceans. Moyle (2002) points out that the diet of small topsmelt (4.9 - 5.6 cm) in one estuary consisted primarily of diatoms and filamentous algae (50% by volume), and detritus (29%), with chironomid midge larvae and amphipods comprising an additional 20 percent.

While all of these forage fish may incorporate some amount of primary producers and detritus in their diets, none can be considered exclusively trophic level 2 consumers. California least terns are not species-specific predators; therefore, their overall dietary composition will vary depending on the relative abundance of suitable prey species. At any given time or location, it is impossible to predict whether prey fish are primarily consuming plant material or the trophic level 2 organisms that feed on plant material. In order to adequately evaluate the full potential

impact of the methylmercury TRC on the endangered California least tern, a diet of **100 percent trophic level 3 fish** is assumed.

The FMR for least terns was estimated using Nagy's allometric equation for all birds (*in* U.S. Environmental Protection Agency, 1993):

FMR (kcal/day) = 2.601 × (body weight in g)$^{0.640}$
FMR = 2.601 × 45 $^{0.640}$
FMR = 29.7 kcal/day

The FIR was then calculated using the equation:

FIR = FMR ÷ metabolizable energy from food (ME)

where ME equals the gross energy (GE) from the food type times the assimilation efficiency (AE) of the animal consuming that food. The GE of bony fishes is 1.2 kcal/g wet weight. The AE for birds consuming fish is 79%. Therefore, the ME for the least tern is 0.948 kcal/g fish.

FIR = 29.7 kcal/day ÷ 0.948 kcal/g fish

FIR for California least tern = 0.031 kg wet weight/day

IV.C. California Clapper Rail (*Rallus longirostris obsoletus*):

The California clapper rail (*R. l. obsoletus*) is the largest of the three rail subspecies considered in this evaluation, followed in descending order by the light-footed and Yuma clapper rails (U.S. Fish and Wildlife Service, 1976). In the only literature found for this particular subspecies that provided body weights, nineteen female California clapper rails from south San Francisco Bay were examined as part of a Master's Degree thesis (Albertson, 1995). Weights ranged from 300 to 400 g, with a **mean weight of 346.1 g**. This mean value was used for the calculation of a wildlife value for this subspecies.

The most comprehensive assessment of the California clapper rail diet is presented by Moffitt (1941). Stomach contents from 18 birds were examined and the food items identified and measured as a volumetric percentage. On average, animal matter accounted for approximately 85 percent of the diet, with the remainder composed of seed and hull fragments of marsh cordgrass. Over half (56.5%) of the overall diet was comprised of plaited horse mussels (*Modiolus demissus*). Spiders of the family Lycosidae (wolf spiders) accounted for 15 percent of the diet, while little macoma clams (*Macoma balthica*) (7.6%), yellow shore crabs (*Hemigrapsis oregonensis*) (3.2%), and wom-out nassa snails (*Ilyanassa obsoletus*) (2.0%) were the remaining important dietary items. Worms, insects, and carrion combined accounted for a total of 1.1 percent of the remaining diet found by Moffitt (1941) in the 18 clapper rail stomachs. The importance of crabs in the clapper rail diet was confirmed by Varoujean (1972), who observed

rails eating striped shore crabs (*Pachygrapsus crassipes*).

Although Moffitt (1941) reported that plant matter accounted for approximately 15 percent on average of the clapper rail diets, the author stated that this percentage probably represented the maximum of a vegetable diet. This conclusion was based on the fact that the birds were collected in early February, a time when animal food items would typically be at lowest abundance. However, it is important to note that this reported average for plant food (~15%) was calculated from a wide range of percentages in the 18 birds examined (0% - 58% plant food). As with other omnivorous species, the amount of any particular food item consumed at any given time may vary substantially depending on a number of factors. While clapper rails most likely do not eat a set amount of plant matter daily, it is clear from Moffitt (1941) that vegetation generally constitutes a substantial dietary item over time.

Based on Moffitt's (1941) assumption that his mid-winter gut analyses represented a maximum for vegetation in the clapper rail diet, and the knowledge that clapper rails nest during a time when animal foods would be in greater abundance (mid-March - July) (U.S. Fish and Wildlife Service, 1984), the overall rail diet for this effort is assumed to be 10 percent vegetation and 90 percent animal matter. For the purposes of this evaluation, the vegetation portion of the diet will be considered as food not contributing to the daily ingested dose of methylmercury. Although mercury is known to accumulate in aquatic plants (Gupta and Chandra, 1998; Ellis and Eslick, 1997; Breteler *et al*., 1981), the scientific literature indicates that accumulation is primarily in the roots rather than in the rhizomes or above-ground tissues (Boening, 2000; Breteler *et al*., 1981).

The primary animal foods of clapper rails according to Moffitt (1941) appear to be mussels, wolf spiders, clams, shore crabs, and snails. Mussels and clams are mainly filter-feeders on plankton, which may include zooplankton, and both are designated as trophic level 2.2 (U.S. Environmental Protection Agency, 1995b). However, phytoplankton and detritus make up the bulk of these organism's diets; therefore, mussels and clams are considered trophic level 2 for this evaluation. Although the EPA classifies snails as trophic level 2 organisms (U.S. Environmental Protection Agency, 1995b), the EPA notes that some marine forms are carnivorous. According to Morris *et al*. (1980), the species of nassa snails consumed by clapper rails are primarily herbivorous deposit feeders; however, Morris *et al*. note that at least one San Francisco Bay population is also carnivorous, preying on polychaete worms. This feeding behavior warrants the classification of trophic level 3 for nassa snails consumed by California clapper rails. The EPA views crabs as trophic level 3.3 organisms; however, this assumption was based on larger, more predatory crabs (*e.g.*, blue crabs) consuming small fish, other crabs, molluscs, and other invertebrates (U.S. Environmental Protection Agency, 1995b). The two crab species identified as food for the California clapper rail, *Hemigrapsis oregonensis* and *Pachygrapsus crassipes*, are primarily herbivorous, feeding on algae and diatoms (Morris *et al*., 1980; Roth and Brown, 1980). Therefore, it is more appropriate to classify these crab species as trophic level 2 organisms for this evaluation.

Evaluating the importance of wolf spiders in the clapper rail diet presents a unique challenge.

Spiders are generally classified as trophic level 3 organisms due to their predatory nature (U.S. Environmental Protection Agency, 1995b). Spiders are also generally regarded as terrestrial species, with limited involvement with aquatic food webs. However, wolf spiders are active hunters and those inhabiting the wetland habitats of clapper rails may be preying on trophic level 2 aquatic invertebrates. At least one species in this family, *Arctosa serii*, inhabits the sandy intertidal zone in the Gulf of California and actively preys on amphipods and ground beetles (Roth and Brown, 1980). If the wolf spiders consumed by California clapper rails exhibit the same feeding behavior, this would suggest a direct accumulation pathway, similar to the consumption of a trophic level 3 fish. However, it is unknown what effect the physiological processes involved with the capture and ingestion of spider prey (*e.g.*, venom immobilization, digestion) would have on the bioavailability of any methylmercury in that prey. In addition, although Moffitt (1941) reported wolf spiders comprising up to 73 percent of the animal matter in clapper rail stomachs, the relative importance in the overall diet may be minor. Moffitt's (1941) analyses were based on volumetric percentages, not on mass. The small amount of digestible body mass in spiders, relative to mussels, clams, crabs, and snails, suggests spiders may be an insignificant component of the overall diet and of the daily ingested dose of methylmercury.

For this evaluation, 90 percent of the California clapper rail diet is assumed to be from aquatic animal matter and 10 percent from vegetation. Based on the trophic level analyses presented above, **5 percent of the overall diet is assumed to be from trophic level 3 organisms (*i.e.*, nassa snails) and the remaining 85 percent from trophic level 2 organisms (*i.e.*, mussels, clams, and crabs)**. While these values are not static, and individual birds may consume varying percentages of each food type or additional prey items, this trophic level breakdown represents a reasonable dietary composition for California clapper rails based on the best available information.

Clapper rails may consume a wide variety of foods. Values for the gross energy content for some of these foods (*e.g.*, shell-less bivalves, shelled crabs) and the efficiency at which rails assimilate them can be found in the *Wildlife Exposure Factors Handbook* (U.S. Environmental Protection Agency, 1993). However, because rails do not consume set amounts of these food types, FIR must be estimated using one of the generic allometric equations from Nagy (2001). Out of the 17 avian categories for predicting FIRs presented by Nagy (2001), Charadriiformes is the taxonomic order most closely related to rails (Gill, 1995). In addition, the rail's feeding ecology most closely resembles that of birds in the Charadriiformes category (*i.e.*, shore birds, gulls, auks). Therefore, the FIR for California clapper rails was calculated using the following equation:

FIR (wet weight) = $1.914 \times (\text{body weight in g})^{0.769}$
FIR = $1.914 \times 346.1^{0.769}$
FIR = 171.63 g/day wet weight

FIR for California clapper rail = 0.172 kg wet weight/day

IV.D. Light-footed Clapper Rail (*Rallus longirostris levipe*):

As the light-footed clapper rail is smaller than the California clapper rail (U.S. Fish and Wildlife Service, 1976), the body weight for the California rail was not considered appropriate for this subspecies. No subspecies-specific information on body weights was found in the scientific literature. Dunning (1993) reported an average weight of 271 g for seven female clapper rails (*R. longirostris*, unidentified subspecies) from South Carolina. While an average body weight for the light-footed subspecies may be slightly more or less than the average reported by Dunning (1993), this value (**271 g**) was used in the calculation of a wildlife value in this effort.

Light-footed clapper rails occupy coastal marsh habitats, similar to the California clapper rail. The most robust documentation of the light-footed clapper rail's diet is presented by Zembal and Fancher (1988). Through direct observations of foraging and from analyses of food materials regurgitated by light-footed clapper rails, a list of prey items were identified. Observations of foraging revealed that clapper rails hunted in marsh vegetation over 90 percent of the time. During these foraging bouts, rails focused on invertebrates at the base of plants or under dried pieces of vegetation and debris. According to the observations of successful capture and swallowing, rails consumed hundreds of these invertebrates per hour. These small organisms could not be identified but appeared to be very mobile, as they would scatter rapidly when discovered by the rails. Due to the amount of time rails foraged on these organisms and the large numbers swallowed during foraging bouts, the researchers concluded that these invertebrates were important dietary items.

When not foraging in vegetation, rails would switch strategies and hunt tidal creek banks, mudflats, and open water. Rails were observed catching and swallowing various shore crabs (*i.e., Pachygrapsus crassipes, Hemigrapsus oregonensis*) and fiddler crabs (*Uca crenulata*) from the creek banks. Both fish (*i.e.*, longjaw mudsucker - *Gillicthys mirabilis*) and ribbed horse mussels (*Ischadium demissum*) were taken from the mudflat habitats. However, observations of foraging on the mussels suggests that only portions of the animals were consumed, as the mussels would close upon first attack and rails appeared unable to reopen them. Other rails in open water were seen capturing California killifish (*Fundulus parvipinnis*) and tadpoles of the Pacific treefrog (*Hyla regila*). Scavenging on fish carcasses was also observed, although the rails may have been eating insect larvae on the carcasses.

Examination of regurgitated pellets provided additional information on clapper rail diets. The most abundant items were the remains of the shore crab species mentioned above. The next most abundant items were the remains of California horn snails (*Cerithidea californica*) and salt marsh snails (*Melampus olivaceous*). Other animal remains identified in regurgitated pellets included crayfish, beetles, isopods, and decapods. These additional items were not ranked according to abundance, although regurgitated pellets collected along a freshwater ditch were composed primarily of crayfish exoskeletons. Plant remains were rare in the regurgitated pellets, with the exception of two pellets that contained 75 elderberry seeds (representing about 25 fruits). The only other plant remains were three small unidentified seeds and several cordgrass seeds. The

researchers noted that only three clapper rails were ever observed feeding on plants, two consuming tips of pickleweed stems and one extracting and swallowing pith from broken cordgrass stems.

Light-footed clapper rails appear similar to other omnivorous birds in that a wide range of both plant and animal foods may be included in the diet, the composition of which may vary depending on any number of environmental or physiological factors. No information was provided by Zembal and Fancher (1988) regarding the percentage of specific food items in the rail diet; however, the authors offered some conclusions about the relative importance of certain organisms. Crabs and snails were considered important prey because of their large size and abundance in rail habitats. The two shore crabs and two snails identified above as prey for clapper rails are all trophic level 2 organisms, feeding on plants or detritus (Morris *et al*., 1980). Fiddler crabs feed primarily on detritus (Barnes, 1980; Kozloff, 1990); therefore, they are also considered trophic level 2 organisms. The small invertebrates consumed by clapper rails were also considered important in the diet because of the large numbers eaten and the amount of time rails spent foraging on them. Although these invertebrates could not be identified by the researchers, the small size of the animals and their tendency to cluster in large concentrations indicates that they should be classified as trophic level 2 organisms.

Zembal and Fancher (1988) did not offer any conclusions regarding the importance of other dietary items such as fish, mussels, tadpoles, and crayfish. However, they observed rails capturing fish numerous times and suggested that fish consumption may be more common than their results would indicate. The two fish species identified as prey, California killifish and longjaw mudsucker, are trophic level 3 predators (Moyle, 2002). In addition to trophic level 3 fish, crayfish were identified in pellets regurgitated by clapper rails. The EPA classifies crayfish at an intermediate trophic level (2.4), noting that crayfish are primarily herbivorous and that animal food is a minor part of the diet if vegetation is available (U.S. Environmental Protection Agency, 1995b). However, Slotton *et al*. (2000) found that signal crayfish (*Pacificasticus leniusculus*) in California can accumulate mercury to high concentrations, similar to predatory fish. While *P. leniusculus* is in a different genus than those identified in the pellets regurgitated by light-footed clapper rails, the omnivorous nature of all crayfish indicates the potential for a greater reliance on animal food than on plant material. For this evaluation, a higher intermediate trophic level (*i.e.*, 2.8) was assigned to crayfish consumed by light-footed clapper rails. Assuming 10 percent of the overall diet is crayfish, 8 percent of this contribution was assigned to trophic level 3 and 2 percent to trophic level 2 (*i.e.*, TL2.8 = 80% TL3, 20% TL2). Further assuming the trophic level 3 fish prey contributes 10 percent of the diet, a total of 18 percent of the overall diet was assigned to trophic level 3 (*i.e.*, 8% from crayfish, 10% from fish).

As noted above, plants appeared to play a minor role in the light-footed clapper rail diet, with the exception of elderberry fruits near a freshwater ditch (Zembal and Fancher, 1988). The fact that rails were only seen eating vegetation by the researchers on three occasions, despite approximately 180 hours of visual contact between March 1979 and August 1987, indicates that vegetation may be an insignificant food source, relative to the overall diet. For this reason, the

breakdown of dietary trophic level composition is based on an assumption of 100 percent animal foods.

The predominant foods of the light-footed clapper rail appear to be trophic level 2 crabs, snails, and small invertebrates. Other important foods, from a bioenergetic standpoint, include trophic level 3 fish and crayfish. Although no specific information was found regarding the percentage of each trophic level contributing to the overall diet, a reasonable assumption of **82 percent trophic level 2 and 18 percent trophic level 3** was used in the calculation of wildlife values for the light-footed clapper rail.

Although differing from the California clapper rail, in that fish and crayfish are important dietary items and vegetation appears insignificant, the similarly indefinite composition of the light-footed clapper rail's diet requires that FIR be estimated using the same allometric equation (Charadriiformes group) from Nagy (2001). For this effort, the body weight for the light-footed rail was estimated to be 271 g.

FIR (wet weight) = $1.914 \times (\text{body weight in g})^{0.769}$
FIR = $1.914 \times 271^{0.769}$
FIR = 142.2 g/day wet weight

FIR for light-footed clapper rail = 0.142 kg wet weight/day

IV.E. Yuma Clapper Rail (*Rallus longirostris yumaensis*):

The Yuma clapper rail is considered smaller than the both the California and light-footed clapper rails (U.S. Fish and Wildlife Service, 1976). However, there was no defensible way to determine a lower body weight for the Yuma rail than the one used for the light-footed rail. No subspecies-specific information on body weights was found in the scientific literature. Subsequently, the **average body weight of 271 g** reported by Dunning (1993) was used in the calculation of a wildlife value in this effort.

The Yuma clapper rail is unique from other clapper rail subspecies in that it resides and breeds in freshwater marshes (Anderson and Ohmart, 1985). Early literature on Yuma clapper rails suggested that the majority of the birds wintered in brackish marshes along the western coast of Mexico and then returned to their freshwater breeding grounds in the U.S. along the Colorado River and the Salton Sea for the spring and summer nesting period (U.S. Fish and Wildlife Service, 1976; Anderson and Ohmart, 1985). Both the California and light-footed clapper rails are considered non-migratory, although the California clapper rail is known to "wander" from its breeding grounds in fall and early winter (U.S. Fish and Wildlife Service, 1976). The Yuma clapper rails that did overwinter in freshwater habitats in the U.S. were considered a small part of the overall population (U.S. Fish and Wildlife Service, 1976; 1983). One possible explanation given for this migratory behavior was that it was in response to reduced food resources in the winter months (Anderson and Ohmart, 1985). However, radio telemetry work conducted

between February 1985 and December 1987 revealed that at least 70 percent of the population along the lower Colorado River remains resident (Eddleman, 1989). Therefore, the dietary information for birds residing in freshwater marshes is assumed on a year-round basis.

Comprehensive dietary information was presented by Ohmart and Tomlinson (1977), who examined stomach contents from 11 Yuma clapper rails collected from California and Arizona. Four birds from the Colorado River Delta in Mexico were also examined. Crayfish (*Procambarus* spp. and *Oropectes* spp.) were by far the most dominant prey items in the nine birds collected from along the Colorado River, averaging 95 percent by volume (range: 80-100%) of the stomach contents. Other food items included various insects, spiders, and molluscs. A small mammal bone was found in one stomach and plant seeds in another. Of the two birds collected from the confluence of the Gila and Colorado Rivers, one stomach contained an introduced freshwater clam (*Corbicula* sp.) (98%) and the other contained isopods (97%). The remaining food items in these two stomachs were unidentified insect parts. The birds collected in Mexico showed a more diverse food assemblage, with the predominant foods being water beetles (56%) and unidentified fish (32%). Fish do not appear to be important dietary items outside of the river delta habitats. A small amount of vegetative matter was also found in these birds, although plant matter appears to play an insubstantial role in the diet for all birds.

The trophic level dietary composition for Yuma clapper rails is based on 100 percent animal foods. It is clear that Yuma clapper rails residing along the Colorado River rely heavily on various freshwater crayfish. While it was once thought that these crayfish became dormant during the winter months, precipitating migratory behavior in the rails, evidence indicates that crayfish are present year-round in at least some locations and reproduce in autumn and early winter (Eddleman, 1989). As noted above in the analysis for light-footed clapper rails, crayfish are considered trophic level 2.8 organisms for determining the dietary composition. However, it is unlikely that Yuma clapper rails feed exclusively on crayfish, based on evidence that the birds supplement their diets with other foods ranging from terrestrial and aquatic insects to molluscs, depending on location and availability. Some of these supplemental food items may be aquatic (*e.g.*, isopods, damselfly nymphs, molluscs) or removed from the aquatic ecosystem (*e.g.*, grasshoppers, weevils, ground beetles). Assuming a reasonable high volume diet of 90 percent crayfish, 72 percent of this contribution can be assigned to trophic level 3 and 18 percent to trophic level 2 (*i.e.*, TL2.8 = 80% TL3, 20% TL2). Based on the dietary assessment provided by Ohmart and Tomlinson (1977), the diet for the Yuma clapper rail can therefore be assumed as **72 percent trophic level 3 organisms (from crayfish), 23 percent trophic level 2 organisms (from crayfish and other TL2 foods), and 5 percent non-aquatic organisms**.

The FIR for Yuma clapper rails was estimated using the same allometric equation (Charadriiformes group) from Nagy (2001). For this effort, the body weights for all three clapper rail subspecies were estimated to be equal (271 g). Therefore, the FIR calculation for the Yuma clapper rail will be identical to the one for the California and light-footed clapper rails.

FIR (wet weight) = 1.914 × (body weight in g)$^{0.769}$
FIR = 1.914 × 271$^{0.769}$
FIR = 142.2 g/day wet weight

FIR for Yuma clapper rail = 0.142 kg wet weight/day

IV.F. Western Snowy Plover (*Charadrius alexandrinus nivosus*):

Snowy plovers are small shorebirds weighing from 34 - 58 g, ranging in length from 15 - 17 cm (U.S. Fish and Wildlife Service, 2001). Dunning (1993) reports a mean weight of 41.4 g from 38 specimens of *Charadrius alexandrinus* (unknown gender) from California, with a range from 37 - 49 g. No information was found indicating gender-specific differences in weight. Therefore, **a weight of 41 g** was used in the calculation of wildlife values for western snowy plovers.

The snowy plover diet consists primarily of aquatic and terrestrial invertebrates (Page *et al*., 1995), with little quantitative information about specific food habits (U.S. Fish and Wildlife Service, 2001). A wide variety of food items are reported for coastal birds: mole crabs, crabs, polychaetes, amphipods, tanaidaceans, flies, beetles, clams, and ostracods (Page *et al*., 1995). Plovers on beaches forage above and below the mean high-tide line, gathering invertebrates from the sand surface, kelp, foredune vegetation, and marine mammal carcasses (Page *et al*., 1995). Flies, beetles, moths, and lepidopteran caterpillars were taken by birds at San Francisco Bay salt-evaporation ponds (Page *et al*., 1995). Plovers in California have been observed pecking small flying insects from mid-air (U.S. Fish and Wildlife Service, 2001), and are known to charge with open mouth into aggregations of adult flies (Page *et al*., 1995).

Tucker and Powell (1999) examined snowy plover fecal samples from a southern California coastal breeding site. Results indicated that the primary prey were terrestrial insect families (*i.e.*, various flies and beetles), although mole crab and nassa snail parts were also identified. Insect larvae were found in 25 percent of the fecal samples. The authors concluded that their results were consistent with findings from other snowy plover diet studies in that the major prey items are flies and beetles. However, the authors noted that polychaete worms are digested too completely to be identified by their technique, and stated that these worms may be important prey items.

Although it appears that snowy plovers mainly feed on non-aquatic insects, of both larval and adult forms, at least some aquatic organisms are included in the diet. These aquatic prey (mole crabs, nassa snails, polychaete worms, amphipods, ostracods, clams, tanaidaceans) can all be classified as trophic level 2 organisms based on their diets (U.S. Environmental Protection Agency, 1995b; Morris *et al*., 1980). For this evaluation, an assumption was made that **trophic level 2 organisms constituted 25 percent** of the overall snowy plover diet. The remaining portion of the diet **(75%) was assumed not to be significantly contributing to the daily ingested dose of methylmercury**. Additional research into the possible relationship between methylmercury in an aquatic system and its bioavailability to terrestrial insects may remove some

of the uncertainty in this assumption.

Due to the wide variety of potential prey items and the subsequent variability in gross energy content and assimilation efficiencies, the FIR for snowy plovers was determined using Nagy's (2001) allometric equation for Charadriiformes (shore birds, gulls, auks):

FIR (wet weight) = $1.914 \times (\text{body weight in g})^{0.769}$
FIR = $1.914 \times 41^{0.769}$
FIR = 33.3 g/day wet weight

FIR for western snowy plover = 0.033 kg wet weight/day

IV.G. Bald Eagle (*Haliaeetus leucocephalus*):

The bald eagle was a representative species used for the derivation of wildlife criteria in the aforementioned GLI (U.S. Environmental Protection Agency, 1995c). For that effort, the bald eagle body weight used in criteria calculations (4.6 kg) was based on the mean of average male and female eagle body weights, although it was noted that female eagles are approximately 20 percent heavier than males. As the avian reference dose for methylmercury is based on adverse reproductive effects manifested by laying females, it is more appropriate to use average female body weights in the calculation of wildlife values.

In the GLI, the EPA presented an average body weight of 5.2 kg for female bald eagles. This value was based on the weights of 37 birds, taken from Snyder and Wiley (1976). Dunning (1993) presented an average female body weight of 5.35 kg, also based on the weights of 37 birds, taken from Palmer (1988). Taking both values into consideration, a **body weight of 5.25 kg** was used in the calculation of wildlife values for this evaluation.

The bald eagle diet has been extensively studied throughout the country. Although generally known as a piscivorous species, bald eagles are opportunistic predators and carrion scavengers (Buehler, 2000). Various birds, mammals, reptiles, amphibians, and crustaceans may serve as additional bald eagle prey (Buehler, 2000). As explained in the introduction to this section, FIRs can be most accurately estimated for an animal consuming different food types (*e.g.*, fish and birds) when there is information about the metabolic energy available from these foods and a reliable estimate of the amount of each food type consumed daily (*e.g.*, 75% fish, 25% birds). Information presented in the Wildlife Exposure Factors Handbook (U.S. Environmental Protection Agency, 1993) regarding the metabolizable energy available from various prey types and the ability of bald eagles to assimilate this energy allows for the use of this method to estimate daily food requirements. However, attempting to quantify a specific dietary composition for bald eagles is more difficult than for other species with a narrower range of prey types, and is further confounded by the fact that food preferences may vary both geographically and temporally.

An additional difficulty in calculating a general FIR for deriving the WV for bald eagles arises because the trophic level composition of the diet can also vary substantially between seasons, locations, or individuals. Calculating the FIR based solely on the percentage of various food types in the diet may not result in a WV representative of the greatest risk from methylmercury in the diet. For example, the daily FIR for an eagle with a diet of 95 percent fish / 5 percent birds will be greater than the FIR for an eagle with a diet of 80 percent fish / 20 percent birds (*i.e.*, less energy available from fish prey requires a greater amount consumed to satisfy bald eagle's free-living metabolic rate). The higher FIR, in turn, results in a lower WV, which may seem the most desirable outcome of this methodology. However, if the bulk of the 95/5 diet consists of trophic level 2 fish and terrestrial birds, the methylmercury concentration in the eagle's overall diet will remain substantially below the WV, regardless of the trophic level approach used. By contrast, the higher WV calculated from the 80/20 diet may be substantially exceeded by either trophic level approach if the diet consists primarily of trophic level 4 fish and piscivorous birds.

In this example, using the dietary composition resulting in the lowest WV as a surrogate for all eagles would give the misleading impression that all eagles may be protected (false negative) by the TRC, while using the higher WV would indicate that all eagles may be at risk from the TRC (false positive). However, the goal of this analysis is to evaluate the protectiveness of the two trophic level approaches, using data for birds with the greatest potential for methylmercury exposure through their diet. Therefore, the FIR used to calculate the WV must be based on the most reliable bald eagle diet with the highest combined percentage of trophic level 4 fish and aquatic-dependent avian prey, and the lowest percentage of terrestrial prey (*i.e.*, no connection to methylmercury in the aquatic environment).

The feeding ecology of avian prey of bald eagles is critical for this analysis because prey birds that consume aquatic biota represent an additional exposure pathway for bald eagles, as methylmercury in fish and aquatic invertebrates is biomagnified as it moves through successively higher trophic level organisms. The biomagnification of methylmercury through piscivorous avian prey was factored into the GLI effort, as data showed piscivorous herring gulls (*Larus argentatus*) were an important dietary component (5.6% of the dietary biomass on average) of Lake Superior bald eagles (U.S. Environmental Protection Agency, 1995d). The study used to determine the bald eagle diet for the GLI effort (Kozie and Anderson, 1991) also found various waterfowl in eagle prey remains. These waterfowl species were not considered piscivorous, yet for some, trophic level 2 aquatic biota can constitute a substantial part of their diet. These waterfowl were not included in the GLI estimate of methylmercury exposure, as the bulk of the bird prey component was comprised of herring gulls. However, in areas where bald eagles consume large numbers of these aquatic-dependent birds, the biomagnification of methylmercury from trophic level 2 organisms into waterfowl tissues may contribute substantially to the bald eagle's daily ingestion of methylmercury.

Several efforts to develop protective mercury criteria (*e.g.*, U.S. Environmental Protection Agency, 1997a; Buchanan *et al*., 2001; California Regional Water Quality Control Board - Central Valley Region, 2001) have used the dietary composition developed in the GLI (U.S.

Environmental Protection Agency, 1995c). Using information on bald eagles nesting on islands and along the shore of Lake Superior in Wisconsin (*from* Kozie and Anderson, 1991), and adjustment factors to estimate the relative number of birds and fish delivered to a nest based on the prey remains found under the nest, the EPA determined that 92 percent of the dietary biomass was comprised of fish and 8 percent comprised of birds or mammals. The adjustment factor was developed to account for the inherent error in estimating a dietary composition based solely on the analysis of prey remains. The Kozie and Anderson (1991) study used to determine bald eagle diets reported that fish comprised 50 percent and birds comprised 48.4 percent of the nest site prey remains. However, direct observations of three nests during part of the study period revealed that fish constituted 97 percent of the captured prey. To address this discrepancy, the EPA's adjustment factors (*i.e.*, - the ratios between the number of each prey type found in nest remains and the number of each prey type observed in nest deliveries during the same period) were applied to the prey remain data for all nest sites in the study. This allowed for an estimate of the total number of birds and fish consumed by bald eagles. Then, using standard body weights for the bird and fish species identified, the percentage of biomass for each food type was calculated.

Using this dietary composition of 92 percent fish and 8 percent birds, along with information about the energetic needs of adult eagles and their ability to assimilate the caloric content of these food types, the GLI presented estimates of the amount of each food type ingested daily: 0.464 kg fish and 0.040 kg birds/mammals (U.S. Environmental Protection Agency, 1995c). The fish component of the overall diet was further broken down as 74 percent trophic level 3 (0.371 kg) and 18 percent trophic level 4 (0.0928 kg), based on data indicating the average trophic level for the fish component of Lake Superior bald eagles is 3.2 (*i.e.*, 80% TL3, 20% TL4). The remaining bird/mammal component of the overall diet was delineated as 5.6 percent piscivorous herring gulls (0.0283 kg) and 2.4 percent non-piscivorous other food (0.0121 kg). Although the GLI breakdown of the bald eagle diet has been used as a default composition in subsequent wildlife criteria efforts, studies of bald eagle diets from other parts of the country reveal a wide range of possible composition preferences. Several of these studies are summarized below.

A study of bald eagles in a desert riparian habitat in central Arizona found that fish comprised 77 percent of the total prey remains found under nests (Haywood and Ohmart, 1986). Mammals accounted for an additional 12 percent, birds 11 percent, and reptiles or amphibians 0.6 percent. The same study compared the findings from prey remains with direct observations of prey capture (73% fish, 5% mammals, 1% birds, 4% reptiles or amphibians, and 17% unidentifiable) and found only a minimal difference in percent composition.

By contrast, bald eagles nesting at various sites along the coast of Washington displayed a stronger dietary preference for birds, which accounted for 53 percent of the total prey remains (*N* = 1198) found under nests in three different regions (Knight *et al.*, 1990). Fish comprised 34 percent of the total remains, with mammals (9%) and invertebrates (4%) making up the rest. There were composition differences between the three sites evaluated, but in each case, birds accounted for the majority of food. Birds comprised 78 percent of all prey remains at Olympic

Peninsula nest sites, but down to 48 percent at San Juan Island sites. The researchers also compared their findings from collected prey remains with direct observations of prey delivery (*N* = 47) and concluded that birds were over-represented in prey collections beneath nests and fish were over-represented in observations of prey carried to nests. The high incidence of bird prey remains (53%) during the observation period is in contrast to the frequency of observations in which birds were delivered to the nest (8%). The frequency of observed fish deliveries was high (92%), but was much lower in prey remain collections (44%) during the observation period. Birds may be over-represented in nest collections due to a greater persistence than fish remains in the environment, while over-representation of fish in observations may be due to the relative ease of identification (Mersmann *et al.*, 1992; Knight *et al.*, 1990). However, this study indicates that birds are important prey for coastal bald eagles.

Dietary habits of resident bald eagles from three nesting areas in southcentral Oregon were studied between 1979 and 1983 (Frenzel, 1984). Nest site prey remain collections and direct observations of 16 eagles fitted with radio transmitters were the methods used. The three study areas were Upper Klamath Lake, outer Klamath Basin, and the Cascade Lakes region. Discrepancies between prey remain collections and observations of predation were also found in this study. At the Upper Klamath Lake site, fish comprised only 25 percent of the prey remains but accounted for 62 percent of the observed prey taken during the breeding season. The amount of fish observed taken at this site increased to 69 percent during the post-breeding season, but then dropped to less than 20 percent in fall and winter. Birds became the dominant food during these seasons, accounting for over 82 percent of the observed prey taken. Mammals were observed taken throughout the breeding and post-breeding seasons, but were not observed during the fall and winter. At Wickiup Reservoir in the Cascade Lakes study area, fish accounted for 100 percent of the observed prey taken during the breeding and post-breeding seasons. The same study looked at the diets of wintering-only bald eagles in the Klamath Basin. For these eagles, wintering and staging waterfowl were the primary food source, supplemented with some mammal prey. No fish remains were found in bald eagle castings from communal roosts, and no foraging attempts on fish were observed through the study.

In addition to the above studies, Volume III of *Trophic Level and Exposure Analyses for Selected Piscivorous Birds and Mammals* (U.S. Environmental Protection Agency, 1995b), presented summaries of bald eagle dietary habit studies throughout the U.S. and British Columbia, along with estimated prey trophic levels. The diets presented in these summaries confirm the wide variability of prey types inherent with an opportunistic forager like the bald eagle. While none of the studies described provided one definitive diet composition preferred by bald eagles, they show that fish are generally the predominant food item during the spring and summer breeding seasons. Birds are second in importance, followed by mammals.

As mentioned previously, the dietary composition developed for the bald eagle in the GLI has been used in various places for the derivation of avian wildlife criteria. However, this dietary composition was specifically determined for the aquatic ecosystem of the Great Lakes and may not be an appropriate default for other parts of the country. Califomia supports both wintering

and resident bald eagles, with a broad array of suitable foraging habitats. Because of this variety, eagle diets in California likely span a wide range of possible food types and trophic level combinations. It is not possible in the scope of this analysis to determine all the potential bald eagle diets in California and evaluate them with regard to the trophic level approaches for the methylmercury criterion.

Instead, a weighted risk approach was taken to determine the appropriate eagle diet for calculation of wildlife values. The goal of this approach was to establish a diet based on the highest trophic level composition reasonably likely to occur, from the predominant habitat type characteristic of California's breeding bald eagles. The primary breeding habitats are mountain and foothill forests and woodlands close to reservoirs, lakes, and rivers (California Department of Fish and Game, 2000). Wintering bald eagles can be found in these same habitats throughout the State, but also forage in a variety of different habitats, such as rangelands and coastal wetlands. Basing the diet on the main habitat of resident breeding birds rather than on some other localized habitat used by non-resident birds is a more appropriate method for evaluating potential adverse reproductive effects from the methylmercury criterion, as it is impossible to predict maternal body burdens of methylmercury once wintering eagles reach their breeding grounds outside of California.

Bald eagles are known to nest in several locations and habitat types dispersed throughout California, including in the central and southern Sierra Nevada range, the central coast range, inland southern California, and on Santa Catalina Island. However, most breeding territories are in the northern part of the State (California Department of Fish and Game, 2000). The results of a 1977-1978 study of 95 bald eagle nest sites revealed that 91 percent of the nesting territories were located in five northern counties (Lehman, 1979). A large majority of these nests (87%) were within one mile of a waterbody, and 70 percent of the nests were associated with reservoirs. Two studies of foraging ecology in these characteristic northern California breeding habitats provided detailed assessments of the trophic level composition of bald eagle diets.

Through collection of nest site prey remains, direct observations of foraging eagles, and time-lapse photography of nest activity, the dietary composition was estimated for bald eagles nesting along a hydrologically-regulated section of northern California's Pit River (Hunt *et al.*, 1992). The study area encompassed 24.5 km of reservoirs and 45.8 km of flowing, regulated river. The study took place over a period of two years, with results indicating that fish comprised approximately 87 percent of the total prey items, while birds (9%) and mammals (4%) comprised the remainder. Based on estimates of edible biomass determined from the prey remains around eight nests, the biomass comprised of fish ranged from 43.8 to 92.6 percent. For all nesting eagle pairs, one fish species (Sacramento sucker - *Catostomus occidentalis*) was the dominant prey; however, eagles at one reservoir (Lower Britton) foraged on a greater percentage of cyprinid fish (*e.g.*, hardhead, tui chub, Sacramento pikeminnow) than the other study regions. While trophic levels for various species of *Catostomus* range from 2 to 3 (U.S. Environmental Protection Agency, 1995b), the food of Sacramento suckers can be dominated by algae, detritus, or invertebrates, depending on the size of the fish, location, or time of year (Moyle, 2002). The next

two most important fish species in all study areas were the hardhead (*Mylopharodon conocephalus*) and Sacramento pikeminnow (*Ptychocheilus grandis*). These fish should be classified as trophic level 3 and 4, respectively, based on their diets (Moyle, 2002).

A variety of avian species were identified in the prey remains collected in this study, amounting to 102 individual birds. In terms of edible biomass, the percentage of the diet comprised of birds ranged from 4.9 to 46.3 percent among the eight nests sampled. While the bird species composition or estimated biomass of birds consumed were not presented for each individual study nest, 18 (17.6%) of the total 102 birds identified were piscivorous species. Based on the overall percentage of all birds in the eagle diets (9%), piscivorous birds accounted for roughly 1.6 percent of the total eagle diet (*i.e.*, - $0.09 \times 0.176 \times 100 = 1.58\%$).

While this study (Hunt *et al.*, 1992) presents estimates of the percent biomass for each food type at each study site, including a breakdown for individual fish species, the estimates were based solely on an analysis of prey remains. The prey remains analysis conducted in this study was quite rigorous, in that individual fish scales were included in the collections and used to determine total numbers of fish prey. Other studies of bald eagle diets (*e.g.*, Kozie and Anderson, 1991) relied solely on samples of bones and feathers collected from nest sites. However, in a subset of the entire Hunt *et al*. (1992) study, diets were analyzed for three nests using a comparison of prey remains with time-lapse photographic observations of prey delivered to the nests. The number of fish delivered to the nests during this period ($N = 117$) was almost twice the number estimated from prey remains during the same period ($N = 64$). The biomass estimated from photographic observations of fish prey (55.1 kg) was also substantially greater than the estimate from prey remains (37.6 kg). The authors suggested that some remains may have been dropped or taken from the nests and that other prey items may have been entirely consumed. Further confounding the analysis, the authors reported that a total of 236 prey deliveries were recorded by the time-lapse cameras, yet only the 117 fish deliveries were presented in the journal article. If the 119 unidentified prey deliveries were birds or mammals, this suggests that fish only accounted for 49.5 percent of the diet during the observation period. Although these discrepancies make it difficult to assign a general dietary composition from this study, the author's comparison of prey remains data and photographic observations indicated that larger fish species were not over-represented in prey remains because of larger and more persistent bones, and smaller fish were not under-represented in prey remains because of softer, less persistent bones.

In an expansion of the previous work, prey remains from 56 eagle nesting territories in three major drainage basins (Sacramento-San Joaquin, Lahontan, Klamath) were collected between 1983 and 1992 (Jackman *et al*., 1999). The total study area comprised numerous rivers, lakes, and reservoirs. Over 80 percent of studied nesting territories were near reservoirs, with the remainder on natural lakes. Riverine habitats were also available as foraging sites for all nesting eagles. Prey remains were collected from in and below nests, sometimes during the late nestling stage but primarily after the young had fledged. Sample collections included bones, fur, feathers, and fine nest lining, the latter containing fish scales and fine bones. The authors acknowledged

that the dietary analysis was biased in that it was based exclusively on prey remains (*i.e.*, no comparison of remains with prey deliveries). However, as demonstrated in the earlier Pit River study, the authors noted that their inclusion of fish scale analysis from the nest lining samples helped to mitigate the potential over- or under-representation of certain fish types. In addition, fish scales may have a greater environmental persistence at nest sites than fish bones, which are typically used in prey remain analyses. Although it is commonly suggested that birds and mammals may be over-represented in dietary studies due to a greater environmental persistence of their prey remains compared with fish remains (*i.e.*, feathers vs. bones), the inclusion of fish scales in the dietary analysis may also help to mitigate this potential bias.

From the 56 nesting territories sampled in this study, 2,351 individual prey items were identified. Fish accounted for over 70 percent of both overall prey numbers and total estimated biomass (1,637 kg). The mean standard lengths of the most commonly taken fish were over 30 cm, with the exception of tui chub (28 cm) and brown bullhead (24 cm). Birds contributed approximately 22 percent and mammals less than 6 percent to total prey numbers and biomass. Western pond turtles and crayfish were the only other prey items identified, and contributed insignificant amounts to the overall diet (<1%). The prey composition varied substantially between 19 waterway study groups, with fish accounting for greater than 50 percent of prey numbers and biomass at most locations. However, birds and mammals were the predominant prey at several individual locations isolated from large rivers. Overall, 20 species of fishes, 41 species of birds, and 15 species of mammals were identified from prey remains.

Of the 20 fish species identified (71.2% of total biomass in overall bald eagle diet), the four primary prey species were brown bullhead (*Ameiurus nebulosus*), Sacramento sucker (*Catostomus occidentalis*), common carp (*Cyprinus carpio*), and tui chub (*Gila bicolor*). The majority of the 20 fish species identified should be classified as trophic level 3 consumers based on their diets of trophic level 2 organisms (Moyle, 2002). However, at the body sizes estimated from the prey remain analysis and the dietary habits presented in Moyle (2002), several fish species identified should be classified as trophic level 4 piscivores: Sacramento pikeminnow (*Ptychocheilus grandis*), rainbow trout (*Onchorhyncus mykiss*), largemouth bass (*Micropterus salmoides*), and Sacramento perch (*Archoplites interruptus*). In addition to the identified fish species, numerous other fish remains could only be identified to family: Centrarchidae, Ictaluridae, Cyprinidae, Salmonidae, and Catostomidae. Of these, it can be assumed that the fish prey identified as Salmonidae should be classified as trophic level 4 organisms.

With the exception of largemouth bass, the majority of the Centrarchid prey remains could not be identified to species, although bass (*Micropterus* spp.), smallmouth bass (*Micropterus dolomieui*), sunfish (*Lepomis* spp.), and bluegill (*Lepomis macrochirus*) were noted in the general Centrarchid grouping. It was impossible to assign a single trophic level to the general Centrarchidae dietary contribution, as large bass should be considered trophic level 4 fish and smaller sunfish and bluegills should be considered trophic level 3 fish (Moyle, 2002). Therefore, an intermediate trophic level (*i.e.*, 3.5) was assigned to the non-specific Centrarchidae contribution to the bald eagle diet. This resulted in 50 percent of the "Other sunfish

(Centrarchidae)" grouping assigned to each of trophic level 3 and 4 (*i.e.*, TL3.5 = 50% TL3, 50% TL4).

The two Ictalurids identified in the study [brown bullhead and channel catfish (*Ictalurus punctatus*)] are opportunistic omnivores, consuming whatever prey they can locate. Benthic invertebrates often constitute the majority of the diet for smaller Ictalurids; however, as bullheads and catfish increase in size, small trophic level 3 fish can become the predominant prey item (Moyle, 2002; U.S. Environmental Protection Agency, 1995b). The fish lengths determined from Ictalurid prey remains in this study ranged from 12.9 - 35.6 cm for brown bullhead and 25.1 - 55.1 cm for channel catfish, suggesting that an intermediate trophic level of 3.5 be assigned to all Ictalurids eaten by bald eagles. As with the non-specific Centrarchids, 50 percent of the Ictalurid biomass contribution to the bald eagle diet, whether identified to species or family, was assigned to each of trophic levels 3 and 4.

With the exception of the Sacramento pikeminnow, Cyprinid minnows in California should be considered trophic level 3 (Moyle, 2002). Therefore, the dietary contribution from fish prey grouped under "Unidentified minnows (Cyprinidae)" was assigned as trophic level 3 for this effort. All fish prey under the "Unidentified suckers (Catostomidae)" grouping were assigned as trophic level 3.

Using the intermediate trophic level breakdown for Centrarchids and Ictalurids, together with the other trophic level 4 fish identified from the prey remains, indicates that 12.7 percent of the overall estimated biomass in the entire study area was comprised of trophic level 4 fish. The remainder of the overall fish component to the biomass (58.5%) is classified as trophic level 3.

Of the 41 bird species identified (22.8% of total biomass in overall bald eagle diet), the two most commonly seen in prey remains were American coot (*Fulica americana*) and mallard (*Anas platyrhynchos*), representing 4.2 and 3.2 percent, respectively, of the total estimated biomass. Several of the species identified are exclusively terrestrial (*e.g.*, mountain quail); however, the majority are dependent on the aquatic ecosystem. Several of these aquatic-dependent species are primarily piscivorous: western grebe (*Aechmophorus occidentalis*), gull (*Larus* spp.), pied-billed grebe (*Podilymbus podiceps*), and common merganser (*Mergus merganser*). These piscivorous birds accounted for approximately 5 percent of the total estimated biomass of the bald eagle diet. Eagles also consumed waterfowl (*e.g.*, *Anas* spp., diving ducks, coots) that depend to varying degrees on prey that are considered trophic level 2 organisms (*e.g.*, aquatic invertebrates and zooplankton). These birds contributed approximately 13 percent (including the 4.2% and 3.2% represented by American coots and mallards) to the total estimated biomass in the overall bald eagle diet.

Based on the dietary analysis presented by Jackman *et al*. (1999), and the trophic level assessment provided above, a generic composition for the bald eagle diet can be estimated as 6 percent mammals, 71.2 percent fish (58.5% TL3, 12.7% TL4) and 22.8 percent birds (13.2% TL2 consumers, 4.8% TL3 consumers, 4.8% non-aquatic consumers). These figures represent an

average dietary composition for all bald eagles in the study area. However, the study also presented dietary composition results from 19 separate sub-areas, described as waterway territory groups. The data from these sub-areas do not provide the level of taxonomic detail regarding prey species as was presented for the entire study area, but they do reveal that substantial differences exist between nesting territories in the relative contribution of birds, mammals, and trophic level 4 fish to the bald eagle diet. Trophic level 4 fish constituted over 35 percent of the dietary biomass in several of the sub-areas, while at three different sub-areas, birds contributed over 60 percent of the dietary biomass. At one sub-area, birds and mammals accounted for 70.6 and 24.7 percent, respectively, of the dietary biomass.

The dietary compositions for each sub-area were presented in percent biomass of major prey groups (*i.e.*, fish, birds, mammals), with the fish group further divided into seven categories (*e.g.*, trout, suckers, sunfish). This sub-area breakdown illustrates the broad range of dietary compositions possible in these characteristic bald eagle habitats, and allowed for an estimation of a bald eagle diet with the greatest potential for methylmercury exposure (*i.e.*, the highest percentage of TL4 fish and aquatic-dependent birds, with the lowest percentage of terrestrial prey). Because the data were only presented in terms of major prey groups and broad fish categories, the degree of certainty in estimating specific trophic level diets varied with each sub-area. For example, fish represented by the "Minnow" category could be considered trophic level 3 (*e.g.*, Sacramento blackfish) or trophic level 4 (*e.g.*, Sacramento pikeminnow). Similarly, the general "Bird" category could include any combination of aquatic-dependent and/or terrestrial species. Jackman *et al*. (1999) provided a level of species-specific detail for each sub-area that allowed for a reasonable determination of the trophic composition of each fish category; however, sub-area specific detail for bird prey was lacking. By evaluating the estimated biomass contribution of each bird species for the entire study area, a general percentage breakdown of the three bird types (*i.e.*, TL2 consumers, TL3 consumers, non-aquatic consumers) could be determined and applied to the overall bird contribution to each sub-area. For the entire study area, birds that consume aquatic invertebrates (TL2 consumers) accounted for approximately 58 percent, piscivorous birds (TL3 consumers) accounted for approximately 21 percent, and terrestrial birds (non-aquatic consumers) accounted for 21 percent of the total avian prey biomass. Using this breakdown, the relative contribution of birds in the diet for each sub-area could be delineated. For example, if the percentage biomass of birds for a particular sub-area was reported as 25 percent, the relative contribution of each bird type was delineated as 14.5 percent TL2 consumers (25 × 0.58), 5.25 percent TL3 consumers (25 × 0.21), and 5.25 percent non-aquatic consumers (25 × 0.21).

The data for all 19 sub-areas were analyzed to identify the bald eagle diet with the greatest potential exposure to methylmercury. Prey remains from one eagle pair foraging at the inflow of the North Fork Feather River to the Oroville Reservoir indicated that fish and birds comprised 83 and 17 percent, respectively, of the total dietary biomass. **The fish component of this total was comprised of both trophic level 4 (39%) and trophic level 3 (44%) species. The avian component of this total was comprised of TL2-consuming birds (10%), TL3-consuming birds (3.5%), and non-aquatic consuming birds (3.5%)**. This diet represented the highest

combined percentage of trophic level 4 fish and aquatic-dependent birds from the entire study area.

The bald eagle FIR based on this diet (83% fish / 17% birds) was calculated using the methodology in the aforementioned *Technical Support Document for Wildlife Criteria* (U.S. Environmental Protection Agency, 1995c), wherein the animal's free-living metabolic rate (FMR) is divided by the metabolizable energy (ME) from the animal's prey. The FMR was determined by Nagy's (1987) allometric equation relating FMR for birds to body weight:

$$\text{FMR (kcal/day)} = 2.601 \times \text{body weight (g)}^{0.640}$$
$$\text{FMR} = 2.601 \times 5250^{0.640}$$
$$\textbf{FMR = 625 kcal/day}$$

According to the *Wildlife Exposure Factors Handbook* (U.S. Environmental Protection Agency, 1993), metabolizable energy equals the gross energy (GE) of the food in kcal/g wet weight times the assimilation efficiency (AE) of the consumer. The Handbook gives a GE value of 1.2 kcal/g for bony fishes, while bird GEs are given as either 1.9 (passerines, gulls, terns) or 2.0 (mallard). Although the majority of avian prey species identified in the Jackman *et al.* (1999) study are more closely related to mallards than to the other bird types, the lower value was used in this analysis because the GE for mallards was for consumption of flesh only. The AEs for eagles consuming birds and fish are given as 78 and 79 percent, respectively.

$$ME_{fish} = 1.2 \text{ kcal/g} \times 0.79 = \textbf{0.948 kcal/g fish}$$

$$ME_{birds} = 1.9 \text{ kcal/g} \times 0.78 = \textbf{1.482 kcal/g birds}$$

Following the process in the TSD, if:

Y = grams of birds consumed, and
4.88Y = grams of fish consumed (*i.e.*, 83% fish ÷ 17% birds = 4.88)

then the FIR for each food can be determined by the equation:

$$\text{FMR} = [Y(g) \times 1.482(\text{kcal/g birds}] + [4.88Y(g) \times 0.948 \text{ kcal/g fish}]$$

$$625 \text{ kcal/day} = 1.482Y + 4.626Y$$

$$625 \text{ kcal/day} = 6.108Y$$

$$Y = 102 \text{ g birds consumed/day}$$

$$4.88Y = 498 \text{ g fish consumed/day}$$

The total FIR for bald eagles becomes:

FIR = [102 g birds + 498 g fish]/day
FIR = 600 g wet weight/day

FIR for bald eagle = 0.600 kg wet weight/day

V. SPECIES-SPECIFIC WILDLIFE VALUES

Species-specific input parameters, using the RfD generated with a UF_A of 1, and the resulting WVs are presented in Table 2. Table 3 provides WVs using the RfD generated with a UF_A of 3. Wildlife Values were calculated using Equation 6, described previously:

$$\mathbf{WV} = \frac{\mathbf{RfD} \times \mathbf{BW}}{\sum \mathbf{FIR_i}}$$

Table 2. Wildlife Values for Methylmercury Calculated Using Reference Dose Generated with an Interspecies Uncertainty Factor (UF_A) of 1

Species	RfD (mg/kg/day)	Body Weight (kg)	FIR (kg/day)	WV (mg/kg diet)
Southern sea otter	0.018	19.8	6.5	0.055
California least tern	0.021	0.045	0.031	0.030
California clapper rail	0.021	0.346	0.172	0.042
Light-footed clapper rail	0.021	0.271	0.142	0.040
Yuma clapper rail	0.021	0.271	0.142	0.040
Western snowy plover	0.021	0.041	0.033	0.026
Bald eagle	0.021	5.25	0.600	0.184

Table 3. Wildlife Values for Methylmercury Calculated Using Reference Dose Generated with an Interspecies Uncertainty Factor (UF_A) of 3

Species	Alternate RfD (mg/kg/day)	Body Weight (kg)	FIR (kg/day)	WV (mg/kg diet)
California clapper rail	0.007	0.346	0.172	0.014
Light-footed clapper rail	0.007	0.271	0.142	0.013
Yuma clapper rail	0.007	0.271	0.142	0.013
Western snowy plover	0.007	0.041	0.033	0.009

VI. BIOMAGNIFICATION INTO AVIAN PREY OF BALD EAGLES

The next step in the approach was to evaluate the protectiveness of the TRC under each trophic level approach. To do this required the trophic level breakouts (*i.e.*, %TL2, %TL3, %TL4) for the diet of each species of concern, the trophic level concentrations determined in each TRC evaluation approach, and Equation 1:

DC = (%TL2 × FDTL2) + (%TL3 × FDTL3) + (%TL4 × FDTL4)

However, additional information was required to perform this evaluation for the bald eagle. As mentioned previously, bald eagles may consume substantial numbers of birds that feed from the aquatic environment. These aquatic-dependent species may be omnivorous (*i.e.*, - feed to varying degrees on plant matter and trophic level 2 biota) or primarily piscivorous. The biomagnification of methylmercury into these prey birds represents a potentially important additional exposure for bald eagles that must be factored into the estimate of a daily ingested dose. For the GLI effort (U.S. Environmental Protection Agency, 1995d), bald eagle consumption of piscivorous herring gulls (*Larus argentatus*) was included in the criteria derivation because herring gulls in the Great Lakes feed primarily on trophic level 3 fish. The EPA applied a biomagnification factor (BMF) of 10 in the calculation of wildlife criteria to account for the biomagnification from these trophic level 3 fish into herring gull tissues. In effect, the BMF is analogous to a food chain multiplier (FCM) because it represents the amount of methylmercury transfer between a prey organism (TL3 fish) and its predator (piscivorous bird). Although the GLI effort did not consider biomagnification into omnivorous waterfowl, the contribution of methylmercury from this pathway should also be included in the risk assessment

for bald eagles. In order to include the consumption of piscivorous and omnivorous birds in the evaluation for bald eagles, additional terms must be incorporated into Equation 1:

$$DC = (\%TL2 \times FDTL2) + (\%TL3 \times FDTL3) + (\%TL4 \times FDTL4) + (\%OB \times FDOB) + (\%PB \times FDPB)$$

%OB - percent of omnivorous birds (TL2-consumers) in diet
FDOB - methylmercury concentration in omnivorous bird prey
%PB - percent of piscivorous birds in diet
FDPB - methylmercury concentration in piscivorous bird prey

As the two trophic level approaches presented in this evaluation are based only on estimated methylmercury concentrations in aquatic organisms, the terms FDOB and FDPB need to incorporate the biomagnification of methylmercury from the aquatic trophic levels into the tissues of birds consumed by bald eagles. In effect:

FDOB = FDTL2 (concentration in TL2 organisms) × **MOB** (*i.e.*, some BMF value representing biomagnification into omnivorous bird prey)

FDPB = FDTL3 (concentration in TL3 organisms) × **MPB** (*i.e.*, some BMF value representing biomagnification into piscivorous bird prey)

VI.A. Biomagnification Factor for Trophic Level 3 Fish to Piscivorous Bird Prey: **MPB**

The BMF of 10 used in the GLI to represent the biomagnification from trophic level 3 fish into herring gulls was arrived at from data indicating that tissue mercury concentrations in piscivorous birds tends to be from 3 to 12 times higher than the tissue mercury concentrations in the fish that the birds feed on (U.S. Environmental Protection Agency, 1995d). An analysis of the three studies used for the EPA's determination (Vermeer *et al*., 1973; Norheim and Froslie, 1978; and Wren *et al*, 1983) is provided below.

Vermeer *et al*. (1973) examined total mercury residues in herring gull eggs and in breast muscle from 83 ducks (six species) from Clay Lake in western Ontario. Only four of the 83 ducks were adults, the rest being flightless ducklings or immature birds. Many of the immature birds were also flightless. Breast muscle samples from five of the collected birds were also analyzed for methylmercury content. The authors concluded that elevated total mercury residues in herring gull eggs did not affect reproductive success, but no information was provided about methylmercury in herring gull tissues or the gull's prey. No conclusions about BMF values can be drawn from the herring gull portion of this study.

In addition to the duck breast muscle samples, food items were collected from the esophagi and stomachs of three of the duck species and analyzed for total mercury concentrations. These food items included yellow perch (*Perca flavescens*) and shiners (*Notropis* sp.) consumed by common mergansers (*Mergus merganser*), and a variety of aquatic invertebrates consumed by common goldeneyes (*Bucephala clangula*) and hooded mergansers (*Lophodytes cucullatus*). Breast

muscle sampled from the five individual ducks was analyzed for methylmercury, which accounted for 69-99 percent of total mercury concentrations. However, the food items from the three mentioned duck species were analyzed for total mercury, making direct assessments of methylmercury biomagnification difficult. While it is commonly accepted that the majority of mercury in fish muscle is methylmercury, it is unclear whether the same holds true for the various molluscs, crayfish, insects, and annelids found as food items in these ducks. In addition, the information regarding biomagnification from these non-fish prey items into duck tissues would have had limited value for the estimation of a BMF to herring gulls for the GLI.

Ten yellow perch collected from esophagi and stomachs of common mergansers during this study averaged 2.7 mg/kg (range 1.6 - 3.6) total mercury. Common merganser breast muscle was not analyzed for methylmercury, but a mean concentration of 6.79 mg/kg (range 4.4 - 13.1) total mercury was reported from 17 analyzed birds. Assuming the relative proportion of mercury to methylmercury is similar in fish tissue and duck breast muscle, an average methylmercury BMF for these birds would be 2.5. An important consideration in evaluating this BMF, however, is that the birds sampled were either ducklings or sub-adults. If the birds were in a stage of substantial feather growth, much of the ingested methylmercury could have been shunted into the feathers instead of muscle tissue (Elbert, 1996; Wiener *et al*., 2002). Body burdens of methylmercury in adult female muscle tissue prior to egg laying may have been substantially greater than the values reported for ducklings and sub-adults.

In the work of Norheim and Froslie (1978), the degree of methylation and organ mercury distribution in several raptorial species in Norway was examined. While this study provided data on methylmercury concentrations in various raptor tissues and evidence of demethylation in raptor organs, prey items were not evaluated. Because of this data gap, no conclusions can be drawn regarding the biomagnification of methylmercury from the diet into tissues of the raptors examined.

Wren *et al*. (1983) examined the bioaccumulation and biomagnification of 21 naturally occurring elements into abiotic and biotic components in an undisturbed Precambrian Shield lake in Ontario. Among the biotic samples were 5 herring gulls, 20 rainbow smelt (*Osmerus mordax*), and 20 bluntnose minnows (*Pimephales notatus*), although it is not clear from the report whether all 20 of the minnows were analyzed. Breast muscle samples from the herring gulls and dorso-lateral muscle samples from the fish were analyzed for mercury. It appears from the report that analysis was for total mercury; however, as has been discussed previously, mercury in fish and avian muscle tissues is primarily methylmercury. This allows for a reasonable estimation of a methylmercury BMF. Average mercury concentration in herring gull breast muscle was 1.7 mg/kg (range 0.66 - 4.0). Average concentration in bluntnose minnow muscle was 0.12 mg/kg (range 0.05 - 0.26), and in rainbow smelt the average concentration was 0.32 mg/kg (range 0.15 - 0.67). The mean length of collected rainbow smelt and bluntnose minnows was 17.3 and 7.4 cm, respectively.

The authors of this study (Wren *et al*., 1983) offered no indication of what the sampled herring gulls preyed upon, except to say that the gulls would "...generally feed on small fish which contain relatively low Hg levels." Herring gulls in the lower Great Lakes were reported to feed primarily on alewife and smelt, with females feeding more on the smaller smelt (mean length: 9 cm) and males feeding more on alewife (mean length: 16 cm) (U.S. Environmental Protection Agency, 1995c). If female herring gulls on the Wren *et al*. (1983) study lake preyed primarily on the smaller bluntnose minnows, a BMF of 14.2 can be calculated (*i.e.*, 1.7 mg/kg in gull breast muscle divided by 0.12 mg/kg in minnow muscle). However, if rainbow smelt are the primary prey, a BMF of 5.3 is calculated (*i.e.*, 1.7 mg/kg divided by 0.32 mg/kg). Taking the average of these two values results in a BMF just under 10, the BMF used by the EPA in the GLI effort.

There has been a great deal of research over the past several decades examining the relationship between dietary mercury concentrations and the resultant concentrations in avian tissues. Controlled laboratory feeding studies, as well as field studies examining mercury concentrations in bird tissues and in the organisms the birds generally feed on, can provide data with which BMFs can be calculated. However, these studies typically are designed to evaluate mercury concentrations in individual tissues such as the liver, kidney, feathers, blood, or brain. While these types of data, and the information they generate regarding biomagnification, are extremely valuable in understanding the toxicokinetics and toxicodynamics of mercury in the exposed bird, they are of limited value for determining BMFs from food into a "whole body" concentration. Whole body concentrations are needed when evaluating the consumption of exposed birds by a predator such as the bald eagle. Ideally, all edible tissues of a dosed bird would be analyzed to provide the averaged methylmercury concentration for the entire bird. Then, knowing the methylmercury concentration in the food, the most accurate BMF for the consumer can be calculated.

Lacking studies where all edible tissues of an exposed bird are analyzed, the most appropriate BMF when considering consumption of the exposed bird by a bald eagle should be based on the relationship between concentrations in the muscle of the test bird and the concentrations in its food. Muscle tissue represents the majority of edible matter in a consumed bird; the pectoralis major and supracoracoideus muscles of the breast by themselves account for between one-fifth and one-third of body weight in flying birds (Proctor and Lynch, 1993). Therefore, methylmercury concentrations in muscle should serve as the best surrogate for whole body concentrations. Muscle tissue concentrations may underestimate the actual whole body concentration, as methylmercury levels in other tissues may be substantially higher; however, the relatively small contribution of these other tissues to the overall edible mass should help to minimize these differences.

As described, two of the studies used to determine a BMF in the GLI effort for trophic level 3 fish to piscivorous birds examined muscle tissues in the target birds. While these studies provide some information regarding mercury biomagnification into piscivorous birds that could be consumed by bald eagles, there was sufficient uncertainty in their extrapolation of BMFs to warrant further analysis for this current effort. An attempt was made to find data directly

connecting methylmercury concentrations in documented food items to methylmercury concentrations in the muscle tissue of adult piscivorous birds.

The work done by Henny *et al*. (2002), previously discussed in Section IV.C (Determination of Test Doses), provided an assessment of mercury in the food and tissues of three piscivorous birds nesting along the lower Carson River in Nevada. Various tissues from both adult and juvenile double-crested cormorants (DCC), black-crowned night-herons (BCNH), and snowy egrets (SE) were analyzed, including methylmercury concentrations in stomach contents. Based on stomach content analyses, it was determined that mean total mercury concentrations in the diets of the three species in 1998 were 0.515 mg/kg (BCNH), 0.905 mg/kg (SE), and 1.44 mg/kg (DCC). Methylmercury accounted for most of the mercury detected, with mean concentrations of 0.48 mg/kg (BCNH), 0.775 mg/kg (SE), and 1.18 mg/kg (DCC).

In 1998, total mercury was measured in liver, kidney, brain, blood, and feathers of all three species examined. Using these concentrations and the data for total mercury in stomach contents, it is possible to calculate total mercury BMFs for each of these specific tissues. However, these values do not allow for an estimate of whole body methylmercury concentrations for two reasons: 1) mercury found in the liver and kidney samples was predominantly inorganic due to postabsorptive demethylation, and 2) the relative contribution of the analyzed tissues to the total edible biomass of each bird is small compared to the contribution of muscle tissue. Although no muscle tissue from any of the bird species was analyzed in this study, it was possible to estimate muscle methylmercury concentrations based on an assumed relationship in piscivorous birds between muscle and brain tissue concentrations. Once muscle methylmercury concentrations were estimated for the birds in the Henny *et al*. (2002) study, a methylmercury BMF from food into a whole body concentration could be calculated.

Additional analyses in the Henny *et al*. (2002) study on a small number of BCNH egg, feather, blood, and brain samples confirmed that mercury residues in these types of avian tissues are essentially 100 percent methylmercury. Brain tissue concentrations were selected to establish the relationship with muscle tissue for several reasons: 1.) no egg concentration values were reported, 2.) feathers were only collected from nestling/fledgling birds, 3.) no studies were found in the scientific literature in which both avian blood and muscle tissue were analyzed for mercury, and 4.) scientific studies examining mercury in avian muscle tissues most commonly include liver, kidney, and brain samples in the analyses.

In reviewing the scientific literature for studies reporting tissue mercury concentrations in piscivorous birds, work done by Elbert (1996) and Elbert and Anderson (1998) with western and Clarke's grebes (*Aechomorphorus occidentalis* and *Aechomorphorus clarkii*) in California provided the most useful data for establishing a brain / muscle relationship. Twenty-three adult birds were collected from three California lakes in 1992, with liver, kidney, breast muscle, and brain tissues analyzed for total mercury. All three lakes are representative of the characteristic habitat used for determining the bald eagle diet used in this analysis; however, one of the three (Clear Lake) is known to be impaired by mercury contamination. Of the other two study sites,

Eagle Lake is relatively pristine, while Tule Lake has previously had problems with organochlorine compounds in the eggs of nesting western grebes (Elbert and Anderson, 1998). Neither of these two lakes are known to have elevated mercury concentrations.

For all birds sampled from the three Elbert and Anderson (1998) study lakes, mean muscle and brain mercury concentrations were 0.79 and 0.22 mg/kg, respectively. These results suggest breast muscle mercury concentrations in piscivorous birds are approximately 3.6 times the concentrations found in brain tissues. Examining the data from each lake, however, reveals variations in this ratio. Mean muscle and brain mercury concentrations in birds at Tule Lake were 0.46 and 0.16 mg/kg, respectively, resulting in a ratio of approximately 2.9. At Eagle Lake, the values for muscle and brain were 0.43 and 0.13 mg/kg, resulting in a ratio of 3.3. Mercury concentrations in birds at Clear Lake were substantially higher, with 1.06 and 0.28 mg/kg in muscle and brain tissue, respectively. These data suggest breast muscle mercury concentrations in piscivorous birds at a mercury contaminated site are approximately 3.8 times the concentrations found in brain tissue.

Because the birds examined in the study by Henny *et al*. (2002) were also sampled from mercury contaminated sites, the mean mercury concentrations reported for brain tissues were multiplied by 3.8 to estimate the concentrations expected in breast muscle. Estimated muscle concentrations for the three species are: BCNH - 6.61 mg/kg (brain = 1.74), SE - 8.74 mg/kg (brain = 2.30), DCC - 42.79 mg/kg (brain = 11.26). Taking the estimated muscle concentrations and dividing by mean methylmercury concentrations in the stomach contents for each species provides BMF values.

BCNH:	6.61 mg/kg in muscle ÷ 0.48 mg/kg in food = **13.77**
SE:	8.74 mg/kg in muscle ÷ 0.775 in food = **11.27**
DCC:	42.79 mg/kg in muscle ÷ 1.18 mg/kg in food = **36.26**

The BMFs estimated for night-herons and egrets are similar in magnitude to the value used for the EPA's GLI effort, while the estimated BMF for the double crested cormorant is more than three times the GLI value. One possible reason for this disparity may be the degree of piscivory exhibited by cormorants compared with the other two species. Henny *et al*. (2002) reported that the stomachs of all the cormorants sampled contained only fish, whereas the contents of the night-heron and egret stomachs varied from 100 percent fish to 100 percent aquatic insects. Based on the percentage volume of stomach items for these two species, the average diet for night-herons and egrets was approximately 34 and 49 percent fish, respectively. It is possible that methylmercury biomagnification from fish into avian muscle tissue is substantially greater for those bird species that are almost exclusively piscivorous, such as the double-crested cormorant and belted kingfisher (*Ceryle alcyon*).

While the remains of both double-crested cormorants and belted kingfishers were found at the nest sites examined in the study used to develop the bald eagle diet for this effort (Jackman *et al*., 1999), their contribution to the overall prey biomass was minimal. Therefore, the BMFs

estimated for black-crowned night-herons and snowy egrets served as the more appropriate surrogates for developing the MPB value for this evaluation.

Averaging the estimated BMFs for the black-crowned night-heron and snowy egrets results in an **MPB** value of **12.5**, used in this evaluation for the bald eagle.

VI.B. Biomagnification for Trophic Level 2 Organisms to Omnivorous Bird Prey: **MOB**

The majority of research on methylmercury and its biomagnification through the aquatic food chain into avian species has focused on piscivorous birds, as the consumption of fish (*i.e.*, higher trophic level biota) represents a pathway with the greatest potential exposure. A review of the scientific literature revealed little that was useful in developing a standardized biomagnification factor for omnivorous waterfowl. However, some data were examined that allowed estimation of a reasonable BMF for this effort.

The Vermeer *et al*. (1973) study discussed in the previous section examined mercury levels in the breast muscle of several species of piscivorous and omnivorous waterfowl, as well as in the stomach contents from individuals of three of these species. Breast muscle samples from 21 common goldeneyes (*Bucephala clangula*), an omnivorous species, showed a mean total mercury concentration of 7.80 mg/kg (range: 0.9 - 19.4). Two individual goldeneyes were further sampled to compare total mercury to methylmercury levels. In these two samples, methylmercury accounted for 73 and 77 percent of the total mercury values. Applying a value of 75 percent methylmercury to the mean total concentration of 7.80 mg/kg results in a mean methylmercury value of 5.85 mg/kg.

Food items from the esophagi and stomachs from seven of the collected goldeneyes confirmed the predominantly invertebrate diet of this species. These food items were analyzed for total mercury; however, the results were reported in a manner that prevents calculation of a precise average concentration. Average total mercury concentrations in the various food items (*e.g.*, bivalves, aquatic insect nymphs, crayfish) ranged from 0.30 to 7.1 mg/kg. Based on the reported values, the average total mercury concentration in the goldeneye diet is approximately 2 mg/kg. As previously noted, making direct assessments of methylmercury biomagnification from this concentration is difficult because it is unknown what percentage of the total mercury in the various invertebrates is methylmercury. In a recent review of mercury ecotoxicology (Wiener *et al*., 2002), the authors point out that the percentage of total mercury present as methylmercury in aquatic invertebrates can vary substantially. Examples of this variation include methylmercury ranging from 9 to 82 percent of total in aquatic insects from northern Wisconsin lakes, and from 20 to 95 percent of total in benthic aquatic insects (detritivores and predatory dragonflies, respectively) from hydroelectric reservoirs in northern Quebec.

With these wide variations possible, the approximate total mercury concentration of 2.0 mg/kg in the goldeneye diet from the Vermeer *et al*. (1973) study could translate into methylmercury

concentrations of 0.18 mg/kg (9% of total) to 1.9 mg/kg (95% of total). Biomagnification factors for the transfer from prey items into goldeneye breast muscle could therefore range from 32.5 (5.85 mg/kg ÷ 0.18 mg/kg) to 3.08 (5.85 mg/kg ÷ 1.9 mg/kg). The true value is likely toward the lower end of the range, as many of the invertebrate prey identified were themselves predatory, possibly resulting in a higher percentage of mercury in the methylated form. However, as discussed previously, an important consideration in evaluating biomagnification from these data is that the birds sampled were either ducklings or sub-adults. If the birds were in a stage of intense feather growth, much of the ingested methylmercury could have been shunted into the feathers instead of muscle tissue (Elbert, 1996; Wiener *et al*., 2002). In addition, body burdens of methylmercury in adult female muscle tissue prior to egg laying may have been substantially greater than the values reported for ducklings and sub-adults.

In an expansion on the previous study, Fimreite (1974) examined 184 piscivorous and omnivorous waterfowl specimens from five different lakes in the same locale of northwestern Ontario. Liver, breast muscle, and stomach contents from twelve of these birds, including three common goldeneyes representing predominantly invertebrate feeders, were analyzed for total and methylmercury. Invertebrates from the three goldeneye stomachs were not identified; however, the contents of each bird were analyzed separately. Methylmercury concentrations in these stomach contents were reported as 0.09, 0.19, and 0.36 mg/kg. These values represented 100, 56, and 47 percent, respectively, of total mercury concentrations. The corresponding breast muscle samples contained 0.11, 0.23, and 0.51 mg/kg methylmercury. For each bird, the reported values indicate biomagnification from diet into breast muscle is only slightly greater than 1 (~ 1.2 - 1.4).

Although life stage was not reported, the three birds sampled were most likely adults. In a separate component of this study, breast muscle and liver from 12 adult and 3 duckling goldeneyes were analyzed for methylmercury. Results showed that mean methylmercury concentrations in duckling breast muscle (7.10 mg/kg) were substantially higher than in adult breast muscle (0.76 mg/kg). While the data suggest biomagnification from food into adult goldeneye breast muscle is low, the timing of sample collection may have masked a greater level of biomagnification prior to the study than indicated from the results. Birds for this study were collected during the periods 20 July - 5 August 1970 and 20 June - 28 July 1971. These periods coincide with the periods of greatest postnuptial molt of goldeneyes in central Ontario, as well as the late stages of duckling growth (Eadie *et al*., 1995). It is possible that adult body burdens of methylmercury were being depurated into replacement feathers, while the young may have finished producing their adult plumage and were no longer eliminating ingested methylmercury through this pathway. Biomagnification into muscle tissue during non-molt periods or after cessation of juvenile feather growth may be substantially greater. If these late stage ducklings were consuming invertebrates with the same methylmercury concentrations as observed in adult stomach contents, biomagnification factors from food into breast muscle could range from approximately 20 to 80 (*e.g.*, 7.10 mg/kg ÷ 0.9 mg/kg = 78.8).

Depuration of methylmercury into growing feathers, excretion in the feces, and deposition into eggs are the principal means of mercury elimination in adult female birds (Wiener *et al*., 2002).

For many of the omnivorous waterfowl species that would be consumed by California bald eagles, molting and egg laying would occur in the spring and summer on northern breeding grounds outside of California. Such was the case with the common goldeneyes in both of the above studies (Vermeer *et al.*, 1973; Fimreite, 1974). Although neither study was designed to determine biomagnification factors, the data they generated could considerably underestimate the extent of biomagnification in California birds.

In order to minimize this potential underestimation, an attempt was made to find data for omnivorous birds in California waters. Eared grebes (*Podiceps nigricollis*) and samples of their invertebrate prey were collected from Eagle Lake, California (Eagles-Smith *et al.*, in prep.). Eagle Lake, a relatively pristine body not known to have substantial mercury contamination, is the same location where Elbert and Anderson (1998) examined western and Clarke's grebes. This is a breeding area for eared grebes, while their wintering habitats are Pacific coastal regions, southwestern United States, Baja California, and Mexico (Cullen *et al.*, 1999).

In the Eagle Lake work, six adult (3 male, 3 female) and three juvenile birds were collected between August and September of 2000. All adults had completed breeding, and were flightless at the time of collection (*i.e.*, both primary and body feather molt). As with the previous two studies discussed, feather replacement during this molt cycle could be an important elimination pathway for the bird's methylmercury body burden. Breast muscle from each bird was sampled and analyzed for total mercury. Concentrations ranged from 0.031 to 0.104 mg/kg (converted from dry weight using 71.5% moisture), with an average of 0.069 mg/kg.

Eared grebes are known to feed predominantly on brine shrimp and brine flies at fall staging areas prior to their winter migration (Cullen *et al.*, 1999). However, their diet at freshwater breeding lakes consists mainly of caddisfly and mayfly larvae (~50%), amphipods (~20%), water beetles (~20%), aquatic snails (~10%), and an occasional fish (Eagles-Smith *et al.*, in prep.). Approximately 50 invertebrate samples were collected from Eagle Lake, from locations where grebes were taken, and analyzed for total mercury after being sorted into general taxonomic groups. Based on the general dietary composition presented above, the analytical results were combined in a weighted average approach to provide an overall mercury concentration for the integrated eared grebe diet. The average total mercury concentration for this integrated diet was 0.02 mg/kg dry weight. Using a general value of 75 percent moisture for these aquatic invertebrates results in a wet weight concentration of 0.005 mg/kg total mercury.

Neither the grebe muscle nor invertebrate samples were analyzed for methylmercury. Applying the same value of 75 percent observed in common goldeneyes from the Vermeer *et al.* (1973) study to represent the ratio of total mercury to methylmercury, the average methylmercury concentration in the eared grebe breast muscle was 0.052 mg/kg. As discussed previously, the methylmercury percentage in aquatic invertebrates can vary considerably, depending on factors such as the organism's trophic position. For the invertebrates sampled in the Eagle Lake study, it was estimated that methylmercury accounted for approximately 60 - 70 percent of total mercury (Eagles-Smith *et al.*, in prep). Of the two primary grebe prey items, only the caddisfly larvae are

considered omnivorous, occupying a higher trophic position, while mayfly larvae are strictly herbivorous (Kozloff, 1990). The amphipods and naucorids consumed by grebes may also exhibit varying degrees of omnivory. These higher trophic level prey, combined with the occasional fish, allow for a reasonable justification for using the higher value of 70 percent methylmercury in invertebrates. This results in an average methylmercury concentration in the grebe's invertebrate diet of 0.0035 mg/kg.

Dividing the average grebe breast muscle concentration (0.052 mg/kg) by the average integrated invertebrate diet concentration (0.0035 mg/kg) results in a biomagnification factor for methylmercury of slightly less than 15 (14.86). Considering these data were generated from a time when a substantial amount of the grebe's methylmercury body burden may have been shunted into replacement feathers, non-molt biomagnification may be substantially greater. These data demonstrate that methylmercury biomagnification in omnivorous waterfowl can be substantially higher than previous studies would indicate.

Assigning an omnivorous waterfowl biomagnification factor for this effort was complicated by numerous factors, including the fact that the various species consumed by bald eagles can exhibit widely varying degrees of omnivory. The eared grebe feeds exclusively on animal matter while other species, such as the American coot (*Fulica americana*), Northern pintail (*Anas acuta*), or American wigeon (*Anas americana*), rely on animal foods to a much lesser extent (Brisbin and Mowbray, 2002; Mowbray, 1999; Austin and Miller, 1995). For every eagle prey bird like the eared grebe having a biomagnification factor of 15 or greater, there may be another exhibiting biomagnification at less than a factor of five. The processes of molting and egg production also contribute to the difficulty in estimating muscle concentrations at any given time of year. It would be virtually impossible to determine true field biomagnification for all omnivorous waterfowl consumed by bald eagles; however, given the information presented above, it is reasonable to assign a general biomagnification factor of 10 for that portion of the bald eagle diet consisting of omnivorous waterfowl.

An **MOB** value of **10** was used in the evaluation for the bald eagle.

VII. EVALUATION OF THE HUMAN HEALTH METHYLMERCURY CRITERION

Once these additional terms for the bald eagle were defined, the modified Equation 1 was used to evaluate the human health criterion for all species of concern.

$$DC = (\%TL2 \times FDTL2) + (\%TL3 \times FDTL3) + (\%TL4 \times FDTL4) + (\%OB \times FDOB) + (\%PB \times FDPB)$$

Inclusion of the additional terms for bald eagles did not affect the calculations for the other species evaluated in this effort, as they only resulted in zero values for those components of the equation (*i.e.*, if %OB = 0, then [%OB × FDOB] = 0). The modified Equation 1 yields the expected overall dietary concentration (DC) resulting from the amount of food eaten from each trophic level, in conjunction with the trophic level methylmercury concentrations estimated from

each of the two TRC trophic level approaches. The DC values calculated for each species could then be compared to the species-specific WV concentrations generated using reference doses, body weights, and food ingestion rates. This simple comparison showed whether either trophic level approach will result in dietary concentrations higher or lower than the protective WV. If lower, then it may be assumed that the species should not be at risk from dietary exposure to methylmercury. If higher, it could be assumed that the species would likely have a dietary exposure that may place it at risk for adverse effects from methylmercury toxicity. In these latter instances, the methodology outlined in the Average Concentration Trophic Level approach can be used to calculate the trophic level-specific methylmercury concentrations necessary to maintain the DC at or below that species' WV.

VII.A. Average Concentration Trophic Level Approach

As explained previously (see Section II.A.), applying the Average Concentration Trophic Level Approach to the TRC of 0.3 mg/kg yields the following trophic level-specific concentrations in aquatic biota:

FDTL2 = 0.029 mg/kg
FDTL3 = 0.165 mg/kg
FDTL4 = 0.66 mg/kg

For the bald eagle, the two biomagnification factors determined previously were used to estimate methylmercury concentrations in the eagle's avian prey:

FDOB = FDTL2 × MOB
FDOB = 0.029 mg/kg × 10
FDOB = 0.29 mg/kg

FDPB = FDTL3 × MPB
FDPB = 0.165 mg/kg × 12.5
FDPB = 2.06 mg/kg

Then, applying these predicted methylmercury concentrations and the trophic level dietary breakouts determined for each species of concern to the modified Equation 1 yielded the total dietary concentrations (DC) presented in Table 4.

Table 4. Predicted Dietary Concentrations (DC) of Methylmercury Under Average Concentration TL Approach

Modified Equation 1:

$$DC = (\%TL2 \times FDTL2) + (\%TL3 \times FDTL3) + (\%TL4 \times FDTL4) + (\%OB \times FDOB) + (\%PB \times FDPB)$$

Species	%TL2	%TL3	%TL4	%OB	%PB	%OF*	DC (mg/kg)
Southern sea otter	0.80	0.20	na	na	na	na	0.056
California least tern	na	1.00	na	na	na	na	0.165
California clapper rail	0.85	0.05	na	na	na	0.10	0.033
Light-footed clapper rail	0.82	0.18	na	na	na	na	0.053
Yuma clapper rail	0.23	0.72	na	na	na	0.05	0.125
Western snowy plover	0.25	na	na	na	na	0.75	0.007
Bald eagle	na	0.44	0.39	0.10	0.035	0.035	0.431

* - The term '%OF' (*i.e.*, other foods) represents dietary items not expected to significantly contribute dietary methylmercury, and is presented in the table only to provide the full dietary composition assessment for each species. These %OF items include plants, terrestrial insects, or avian prey not dependent on aquatic biota. The term was not included in the equation to determine DC values because the assumed absence of significant methylmercury in these food items would only result in a zero value for that component of the equation, thus having no effect on the final DC value:

[%OF × FDOF (methylmercury concentration in other foods)]
[%OF × 0] = 0

The DC values from Table 4., representing the methylmercury concentration in the overall diet of the species resulting from the trophic level-specific concentrations generated by the Average Concentration Trophic Level Approach, were directly compared with the species-specific WVs (Table 5). These comparisons allowed for the presentation of the DC value as a percentage of the corresponding WV, which provided a measure of the protectiveness afforded by the TRC under this approach.

Table 5. Ratio of DC Values to WVs Under Average Concentration TL Approach

Species	DC Values	WVs*	Ratio (DC/WV)
Southern sea otter	0.056	0.055	102%
California least tern	0.165	0.030	550%
California clapper rail	0.033	0.042 (0.014)	79% (236%)
Light-footed clapper rail	0.053	0.040 (0.013)	133% (408%)
Yuma clapper rail	0.125	0.040 (0.013)	313% (962%)
Western snowy plover	0.007	0.026 (0.009)	27% (77%)
Bald eagle	0.431	0.184	234%

* - Values in parentheses represent the WVs generated from the altemative RfD for clapper rails and snowy plover generated using the UF_A of 3, and the subsequent relationships to the DC values.

Wildlife values for the California least tern, light-footed clapper rail, Yuma clapper rail, and bald eagle would be significantly exceeded if their prey contained methylmercury concentrations allowed under the Average Concentration Trophic Level Approach. Wildlife values determined for all three clapper rail subspecies using the alternative RfD would be exceeded under this approach. The WV for the southern sea otter appears as though it would not be significantly exceeded under this approach, while the DC for the western snowy plover would remain well below the WV regardless of the RfD used.

VII.B. Highest Trophic Level Approach

As explained previously (see Section II.B.), applying the Highest Trophic Level Approach to the TRC of 0.3 mg/kg yields the following trophic level-specific concentrations:

FDTL2 = 0.013 mg/kg
FDTL3 = 0.075 mg/kg
FDTL4 = 0.3 mg/kg

For the bald eagle, the two biomagnification factors determined previously were used to estimate methylmercury concentrations in the eagle's avian prey:

FDOB = FDTL2 × MOB
FDOB = 0.013 mg/kg × 10
FDOB = 0.13 mg/kg

FDPB = FDTL3 × MPB
FDPB = 0.075 mg/kg × 12.5
FDPB = 0.94 mg/kg

Then, applying these predicted methylmercury concentrations and the trophic level dietary breakouts determined for each species of concern to the modified Equation 1 yielded the total dietary concentrations (DC) presented in Table 6.

Table 6. Predicted Dietary Concentrations (DC) of Methylmercury Under Highest TL Approach

Modified Equation 1:

$$DC = (\%TL2 \times FDTL2) + (\%TL3 \times FDTL3) + (\%TL4 \times FDTL4) + (\%OB \times FDOB) + (\%PB \times FDPB)$$

Species	%TL2	%TL3	%TL4	%OB	%PB	%OF*	DC (mg/kg)
Southern sea otter	0.80	0.20	na	na	na	na	0.025
California least tern	na	1.00	na	na	na	na	0.075
California clapper rail	0.85	0.05	na	na	na	0.10	0.015
Light-footed clapper rail	0.82	0.18	na	na	na	na	0.024
Yuma clapper rail	0.23	0.72	na	na	na	0.05	0.057
Western snowy plover	0.25	na	na	na	na	0.75	0.003
Bald eagle	na	0.44	0.39	0.10	0.035	0.035	0.196

* - The term '%OF' (*i.e.*, other foods) represents dietary items not expected to significantly contribute dietary methylmercury, and is presented in the table only to provide the full dietary composition assessment for each species. These %OF items include plants, terrestrial insects, or avian prey not dependent on aquatic biota. The term was not included in the equation to determine DC values because the assumed absence of significant methylmercury in these food items would only result in a zero value for that component of the equation, thus having no effect on the final DC value:

[%OF × FDOF (methylmercury concentration in other foods)]
[%OF × 0] = 0

The DC values from Table 6., representing the methylmercury concentration in the overall diet of the species resulting from the trophic level-specific concentrations generated by the Highest Trophic Level Approach, were directly compared with the species-specific WVs (Table 7). These comparisons allowed for the presentation of the DC value as a percentage of the corresponding WV, which provided a measure of the protectiveness afforded by the TRC under this approach.

Table 7. Ratio of DC Values to WVs Under Highest TL Approach

Species	DC Values	WV Values*	Ratio (DC/WV)
Southern sea otter	0.025	0.055	45%
California least tern	0.075	0.030	250%
California clapper rail	0.015	0.042 (0.014)	36% (107%)
Light-footed clapper rail	0.024	0.040 (0.013)	60% (185%)
Yuma clapper rail	0.057	0.040 (0.013)	143% (438%)
Western snowy plover	0.003	0.026 (0.009)	12% (33%)
Bald eagle	0.196	0.184	107%

* - Values in parentheses represent the WVs generated from using the alternative RfD for clapper rails and snowy plover generated using the UF_A of 3, and the subsequent relationships to the DC values.

Wildlife values for the California least tern and Yuma clapper rail would be substantially exceeded if their prey contained methylmercury concentrations allowed under the Highest Trophic Level Approach. The bald eagle WV would only be slightly exceeded by this approach. Using the alternative RfD, the WV for the light-footed and Yuma clapper rails would be substantially exceeded under this approach, while the WV for the California clapper rail would only be slightly exceeded. The DC for the western snowy plover would remain substantially below the WV regardless of the RfD used.

VIII. EVALUATION RESULTS

VIII.A. Southern Sea Otter

The southern sea otter was federally listed as threatened in 1977 (42 Federal Register 2965). Critical habitat for the species has not been designated. A revised recovery plan was published in 2003 (U.S. Fish and Wildlife Service, 2003).

Life History: Generally, the home ranges of southern sea otters consist of several heavily used areas with travel corridors between them. Animals often remain in an area for a long period of time and then suddenly move long distances; these movements can occur at any time of the year. Male southern sea otters have larger home ranges and are less sedentary than females. Juvenile males move further from natal groups than do juvenile females, likely due to territorial and aggressive behavior exhibited toward juvenile males by older males. Most male southern sea otters leave the central portion of the range and travel to its ends during the pupping season, which occurs primarily in the winter and spring (Riedman and Estes, 1990). Southern sea otters mate and pup throughout the year. A peak period of pupping occurs from January to March, and a secondary pupping season occurs in late summer and early fall. Parental care is provided solely by the female. Because of their ability to eat large quantities of marine invertebrates, sea otters play an extremely important role in the nearshore marine community.

Historic and Current Range: Southern sea otters once ranged from the central coast of Baja California north to at least northern California, although they may have ranged as far north as Prince William Sound in Alaska (Riedman and Estes, 1990; Wilson *et al*., 1991). Prior to being protected from hunting for their pelts in 1911, southern sea otters were reduced to only a remnant colony near Bixby Creek along the Big Sur coast in California. Since 1911, the species has expanded north and south from the Bixby Creek colony. Currently, the range of the southern sea otter extends from about Half Moon Bay to Point Conception, with a small translocated colony at San Nicolas Island in southern California.

Rangewide Trends and Current Threats: Historically, the number of southern sea otters was probably between 16,000 and 20,000 (California Department of Fish and Game, 1976). By the end of the 19th century, the sea otter had been hunted nearly to extinction throughout its range. Southern sea otters along the central coast of California experienced a general recovering trend, increasing from as few as 50 animals in 1911 to an estimated 1,789 in 1976. Limitations on set-net fisheries imposed by the California Department of Fish and Game contributed to population increases in the late 1970s and early 1980s (Estes, 1990). Population counts declined from 1995 through 1999 but have since stabilized or increased. During the spring of 2003, a total of 2,505 sea otters were counted.

Current threats to the southern sea otter include disease, exposure to environmental contaminants, intentional take (shooting), and entanglement in fishing gear. Oil spills, which could occur at any time, threaten the southern sea otter with catastrophic decimation or localized

extinction (U.S. Fish and Wildlife Service, 2003).

Evaluation Results: Although the southern sea otter is at risk of exposure to methylmercury from the aquatic organisms in its diet, the analyses performed under each Trophic Level Approach indicate that the EPA's human health TRC (0.3 mg/kg) is not likely to result in a dietary exposure that would place sea otters at risk from methylmercury toxicity (see Tables 5 & 7). Due to the preponderance of trophic level 2 organisms in the otter's diet, neither the Average Concentration nor Highest Trophic Level Approach would result in dietary concentration (DC) values significantly above the calculated Wildlife Value (WV). The DC value generated from the otter's dietary composition and the trophic level methylmercury concentrations determined in the Average Concentration TL Approach is essentially the same as the calculated WV (DC - 0.056 mg/kg, WV - 0.055 mg/kg). The DC value generated in the Highest TL Approach is substantially below the WV (DC - 0.025 mg/kg, WV - 0.055 mg/kg).

VIII.B. California Least Tern

The California least tern was federally listed as endangered in 1970 (35 Federal Register 16047). A detailed account of the taxonomy, ecology, and biology of the California least tern is presented in the approved Recovery Plan for this species (U.S. Fish and Wildlife Service, 1985a).

Life History: California least terns are migratory. They arrive in California in April to breed and depart to wintering areas in Central and South America by the end of September. Little is known about least tern wintering areas. While in California, least tern adults court, mate, and select nest sites; lay, incubate, and hatch eggs; and raise young to fledging prior to departing from the breeding site.

After their eggs hatch, breeding adults catch and deliver small fish to the flightless young. The adults shift their foraging strategy when chicks hatch in order to obtain the very small sized fish suitable for nestlings (U.S. Fish and Wildlife Service and National Marine Fisheries Service, 2000). The young begin to fly at about 20 days of age, but continue to be fed and are taught how to feed by their parents for some time after fledging. Most foraging activity is conducted within a couple miles of the colony (Atwood and Minsky, 1983). After fledging, the young terns do not become fully proficient at capturing fish until after they migrate from the breeding grounds.

Historic and Current Range: The California least tern continues to occupy nesting sites distributed throughout its historic range. The historic breeding range extended along the Pacific Coast from Moss Landing, Monterey County, California, to San Jose del Cabo, southern Baja California, Mexico (American Ornithologists Union, 1957; Dawson, 1924; Grinnell, 1928; Grinnell and Miller, 1944). However, least terns were nesting several miles north of Moss Landing at the mouth of the Pajaro River, Santa Cruz County, California, at least from 1939 (W.E. Unglish, Western Foundation of Vertebrate Zoology egg collection) to 1954 (Pray, 1954); and although nesting at San Francisco Bay was not confirmed until 1967 (Chandik and Baldridge, 1967), numerous spring and summer records for the area suggest nesting may have

occurred previously (Allen, 1934; Chase and Paxton, 1965; Grinnell and Wythe, 1927; Sibley, 1952). Since 1970, nesting sites have been documented in California from San Francisco Bay to the Tijuana River at the Mexican Border; and in Baja California from Ensenada to San Jose del Cabo at the tip of the peninsula.

Rangewide Trends and Current Threats: There are no reliable estimates describing the historic numbers of California least terns along the Pacific Coast (U.S. Fish and Wildlife Service, 1985a). Early accounts describe the existence of substantial colonies along the southern and central California coast (Bent, 1921), including a colony of about 600 breeding pairs along a 3-mile stretch of beach in San Diego County (Shepardson, 1909). At the time of its Federal listing as endangered in 1970, the total U.S. population of the California least tern was estimated to be 600 breeding pairs (U.S. Fish and Wildlife Service and National Marine Fisheries Service, 2000). The dramatic decline in breeding least terns has been attributed to the degradation or loss of breeding sites, colonies, and foraging areas, which resulted from human development and disturbance, and pollution (U.S. Fish and Wildlife Service, 1985a).

The current U.S. population of the California least tern is grouped into 5 geographically discrete clusters, which support multiple active and historic breeding sites. These clusters include: (1) San Diego County, (2) Los Angeles/Orange Counties, (3) Ventura County, (4) San Luis Obispo/Santa Barbara Counties, and (5) San Francisco Bay area. Since its listing, the statewide population of the least tern has reached an estimated 4,009 breeding pairs in 1997 (U.S. Fish and Wildlife Service and National Marine Fisheries Service, 2000). Despite this dramatic increase in breeding pairs, statewide monitoring has revealed threats to the least tern which emphasize the importance of demography to the least tern's survival and recovery.

California least terns were once common along the central and southern California coast. The decline of the California least tern is attributed to prolonged and widespread destruction and degradation of nesting and foraging habitats, and increasing human disturbance to breeding colonies. Conflicting uses of southern and central California beaches during the California least tern nesting season have led to isolated colony sites that are extremely vulnerable to predation from native, feral, and exotic species, overwash by high tides, and vandalism and harassment by beach users. Control of predators constitutes one of the most crucial needs at California least tern nesting sites.

Evaluation Results: In contrast to the evaluation results for the southern sea otter, applying the TRC under either of the trophic level approaches examined here is likely to result in a dietary exposure that may place California least terns at risk for adverse effects from methylmercury toxicity. Due to the tern's relatively small body size and its exclusively piscivorous diet, the WV (0.030 mg/kg) would be significantly exceeded by the DC values generated from the trophic level concentrations under each TL approach. In the case of the Highest TL Approach, the trophic level concentrations would result in a DC value (0.075 mg/kg) 250 percent of the tern's WV (see Table 7). The trophic level concentrations under the Average Concentration TL Approach would result in an even greater DC value (0.165 mg/kg), 550 percent of the WV (see Table 5). While

the extent of any potential adverse effects from either DC value cannot be quantified, the degree of WV exceedance under each TL approach suggests a high probability that dietary methylmercury exposure from the TRC could reach a level at which adverse effects to least terns may be expected. Based on the analyses performed in this effort, methylmercury concentrations in TL3 fish, the tern's sole prey base, would have to be substantially lower than the TL3 concentrations expected under each TL approach in order to maintain dietary exposure at the protective WV for California least terns.

VIII.C. California Clapper Rail

The clapper rail was federally listed as endangered in 1970 (35 Federal Register 16047). A detailed account of the taxonomy, ecology, and biology of the clapper rail can be found in the approved Recovery Plan for this species (U.S. Fish and Wildlife Service, 1984).

Life History: Clapper rails are non-migratory residents of San Francisco Bay tidal marshes. Research in a north San Francisco Bay marsh concluded that the clapper rail breeding season, including pair bonding and nest construction, may begin as early as February (Evens and Page, 1983). Field observations in south San Francisco Bay marshes suggest that pair formation also occurs in February in some areas (U.S. Fish and Wildlife Service and National Marine Fisheries Service, 2000). The clapper rail breeding season has two nesting peaks, one between mid-April and early-May and another between late-June and early-July. Harvey (1988) and Foerster *et al.* (1990) reported mean clutch sizes of 7.27 and 7.47 for clapper rails, respectively. The end of the breeding season is typically defined as the end of August, which corresponds with the time when eggs laid during renesting attempts have hatched and young are mobile.

Historic and Current Range: Of the 193,800 acres of tidal marsh that bordered San Francisco Bay in 1850, about 30,100 acres currently remain (Dedrick, 1993). This represents an 84 percent reduction from historical conditions. Furthermore, a number of factors influencing remaining tidal marshes limit their habitat values for clapper rails. Much of the east San Francisco Bay shoreline from San Leandro to Calaveras Point has undergone erosion, resulting in a potential loss of local clapper rail populations. In addition, an estimated 600 acres of former salt marsh along Coyote Creek, Alviso Slough, and Guadalupe Slough, had been converted to fresh- and brackish-water vegetation marshes due to freshwater discharge from south San Francisco Bay wastewater facilities. Converted marshes are of lower quality for clapper rails.

The suitability of many marshes for clapper rails is further limited, and in some cases precluded, by their small size, fragmentation, and lack of tidal channel systems and other micro-habitat features. These limitations render much of the remaining tidal marsh acreage unsuitable or of low value for the species. In addition, tidal amplitudes are much greater in the south Bay than in San Pablo or Suisun bays (Atwater *et al.*, 1979). Consequently, many tidal marshes are completely submerged during high tides and lack sufficient escape habitat, likely resulting in nesting failures and high rates of predation. The reductions in carrying capacity in existing marshes necessitate the restoration of larger tracts of habitat to maintain stable populations.

Several years ago, the clapper rail population was estimated to be approximately 500 to 600 individuals in the southern portion of San Francisco Bay, while a conservative estimate of the north San Francisco Bay population, including Suisun Bay, was 195 to 282 pairs (U.S. Fish and Wildlife Service and National Marine Fisheries Service, 2000). Historic populations at Humboldt Bay, Elkhorn Slough, and Morro Bay are now extinct; therefore, the 30,100 acres of tidal marsh remaining in San Francisco Bay represent the current distribution of this subspecies.

Rangewide Trends and Current Threats: As described above, the clapper rail's initial decline resulted from habitat loss and degradation, and reduction in range. Throughout San Francisco Bay, the remaining clapper rail population is besieged by a suite of mammalian and avian predators. At least 12 native and 3 non-native predator species are known to prey on various life stages of the clapper rail (Albertson, 1995). Artificially high local populations of native predators, especially raccoons, result as development occurs in the habitat of these predators around the Bay margins (U.S. Fish and Wildlife Service and National Marine Fisheries Service, 2000). Encroaching development not only displaces lower order predators from their natural habitat, but also adversely affects higher order predators, such as coyotes, which would normally limit population levels of lower order native and non-native predators, especially red foxes (Albertson, 1995).

Hunting intensity and efficiency by raptors on clapper rails also is increased by electric power transmission lines, which criss-cross tidal marshes and provide otherwise-limited hunting perches (U.S. Fish and Wildlife Service and National Marine Fisheries Service, 2000). Non-native Norway rats (*Rattus norvegicus*) long have been known to be effective predators of clapper rail nests (DeGroot, 1927; Harvey, 1988; Foerster *et al.*, 1990). Placement of shoreline riprap favors rat populations, which results in greater predation pressure on clapper rails in certain marshes. These predation impacts are exacerbated by a reduction in high marsh and natural high tide cover in marshes.

The proliferation of non-native red foxes into tidal marshes of the south San Francisco Bay since 1986 has had a profound effect on clapper rail populations. As a result of the rapid decline and almost complete elimination of rail populations in certain marshes, the San Francisco Bay National Wildlife Refuge implemented a predator management plan in 1991 (Foerster and Takekawa, 1991) with an ultimate goal of increasing rail population levels and nesting success through management of red fox predation. This program has proven successful in increasing the overall south San Francisco Bay populations from an all-time low; however, it has been difficult to effectively conduct predator management over such a large area as the south San Francisco Bay, especially with the many constraints associated with conducting the work in urban environments (U.S. Fish and Wildlife Service and National Marine Fisheries Service, 2000).

Predator management for clapper rails is not being regularly practiced in the north San Francisco Bay, and rail populations in this area remain susceptible to red fox predation. Red fox activity has been documented west of the Petaluma River and along Dutchman Slough at Cullinan Ranch. Along Wildcat Creek near Richmond, where recent red fox activity has been observed,

the rail population level in one tidal marsh area has declined considerably since 1987, even though limited red fox management was performed in 1992 and 1993 (U.S. Fish and Wildlife Service and National Marine Fisheries Service, 2000).

In addition to habitat loss and predation pressures, pollutants in the aquatic environment appear to be a continuing threat to California clapper rail populations. Schwarzbach *et al.* (in press) examined factors affecting clapper rail reproductive success in San Francisco Bay, including predation, flooding, and contaminant exposure. Both predation and contaminants appeared to contribute to observations of low hatching success and overall fecundity for clapper rail nests in six intertidal salt marshes in the Bay. Egg hatchability was depressed in all marshes, with observations of deformities, embryo hemorrhaging, and embryo malpositions. Failed-to-hatch eggs contained various levels of trace element and organochlorine contaminants, with mercury at elevated concentrations in at least some eggs from all six marshes. The researchers stated that mercury appeared to consistently be the contaminant most likely to produce the low hatchability observed in all marshes sampled.

Evaluation Results: As explained previously in this document, the analyses for all three rail subspecies and the western snowy plover included evaluations using two WVs, based on RfDs generated from different interspecies uncertainty factors (UF_A). The WV calculated for the California clapper rail with the UF_A of 1 is 0.042 mg/kg. Comparing this WV with the expected DC values from the trophic level concentrations under both the Average Concentration TL Approach (DC - 0.033 mg/kg) and the Highest TL Approach (DC - 0.015 mg/kg) indicate that the TRC is not likely to result in dietary exposure that would place California clapper rails at risk for adverse effects from methylmercury toxicity, as both DC values are substantially below the WV (see tables 5 & 7).

However, the WV calculated with the UF_A of 3 (0.014 mg/kg) produces different results. The DC value from the Average Concentration TL Approach (0.033 mg/kg) is 236 percent of this WV, indicating that dietary exposure in California clapper rails may place them at risk under this TL approach. The DC value from the Highest TL Approach (0.015 mg/kg) is only slightly above the WV. The small differential (<10%) between the two is well within reasonable bounds, recognizing the various uncertainties and assumptions inherent in this methodology, to conclude that dietary exposure resulting from applying the TRC under the Highest TL Approach should not place California clapper rails at risk for adverse effects from methylmercury toxicity.

The question of which UF_A is the most appropriate to represent the clapper rail's sensitivity relative to mallard ducks, the species used in establishing the avian test dose (Heinz, 1979), cannot yet be definitively answered. However, data collected in the last decade on California clapper rails in the San Francisco Bay region allows for a parallel evaluation of the protectiveness afforded by the two WV values and the UF_As on which they were based.

Schwarzbach *et al.* (in press) collected failed-to-hatch clapper rail eggs from various marshes around San Francisco Bay in 1991-1992 (south Bay) and 1998-1999 (north Bay). The eggs were

analyzed for a number of pollutants, including mercury. Mean egg total mercury concentrations were then calculated for both south Bay eggs (0.54 mg/kg fresh wet weight, range: 0.17 - 2.52) and north Bay eggs (0.36 mg/kg fww, range: 0.11 - 0.87). A subset of collected rail eggs was analyzed for methylmercury, with results demonstrating that methylmercury was on average 95 percent of the total mercury found. South and north Bay means could then be adjusted to 0.513 and 0.342 mg/kg methylmercury, respectively. The south Bay average is equivalent to the avian 'lowest observed adverse effects concentration' (LOAEC) seen in pheasants (Fimreite, 1971).

In a corollary investigation (Schwarzbach *et al.*, 1996), clapper rail prey organisms (*i.e.*, snails, crabs, mussels) were collected in 1992 and 1994 from the same Bay marshes used in rail egg collections. The prey collections from 1992 were analyzed for total mercury, while those from1994 were analyzed for methylmercury. Only the south Bay marsh collections included all three prey organisms. The mean methylmercury concentration for all prey organisms in the south Bay, assuming 75 percent moisture, was 0.036 mg/kg (range: 0.0357 - 0.0363). This value is lower than the WV (0.042 mg/kg) calculated to be protective of clapper rails using the UF_A of 1.

These data allowed the calculation of a diet-to-egg transfer factor for California clapper rails in south San Francisco Bay. Taking the mean rail egg concentration of 0.513 mg/kg divided by the mean prey concentration of 0.036 mg/kg results in a methylmercury diet-to-egg transfer factor of 14.25. Multiplying the WV (0.042 mg/kg) generated with the UF_A of 1 by the diet-to-egg transfer factor of 14.25 results in an estimated methylmercury concentration in the egg of 0.598 mg/kg, higher than what is presently found in south Bay rail eggs. Multiplying the alternate WV (0.014 mg/kg) generated with the UF_A of 3 results in an estimated methylmercury concentration in the egg of 0.199 mg/kg. Based on the egg injection work discussed previously (Heinz, pers. comm., 2003) and assessments of the rail's current reproductive status (Schwarzbach *et al.*, in press), it has been estimated that a value of 0.2 mg/kg fww methylmercury in rail eggs would be a reasonable and appropriate 'no observed adverse effects concentration' (NOAEC) (Schwarzbach, pers. comm., 2003).

Although these data are limited in that collecting failed-to-hatch eggs does not represent a random sample analysis of methylmercury concentrations, they did provide parallel support that a UF_A of 3 is necessary to determine an appropriately protective RfD (0.007 mg/kg bw/day), and subsequent WV (0.014 mg/kg), for the California clapper rail. Given this additional validation of the higher UF_A, it can then be concluded that applying the TRC only under the Highest TL Approach is necessary to maintain dietary exposure at the protective WV for California clapper rails.

VIII.D. Light-footed Clapper Rail

The light-footed clapper rail was federally listed as endangered on October 13, 1970 (35 Federal Register 16047) and state listed as endangered in California on June 27, 1971. The original recovery plan for this species was approved in July 1979 and a revision was published on June 24, 1985 (U.S. Fish and Wildlife Service, 1985b). Critical habitat has not been designated for

this species.

Life History: Rails use coastal salt marshes, lagoons, and their maritime environs (Zembal, 1989). The birds nest in the lower littoral zone of coastal salt marshes where dense stands of cordgrass (*Spartina foliosa*) are present. They also build nests in pickleweed (*Salicornia virginica*) (Massey *et al*., 1984). Rails have also been known to reside and nest in freshwater marshes, although this is not common (Thelander and Crabtree, 1994). They require shallow water and mudflats for foraging, with adjacent higher vegetation for cover during high water (Zeiner *et al*., 1990). Rails forage in all parts of the saltmarsh, concentrating their efforts in the lower marsh when the tide is out, and moving into the higher marsh as the tide advances (Zembal *et al*., 1989).

The pair bond in rails endures throughout the season, and often from year to year. Nesting usually begins in March and late nests have usually hatched by August. Nests are placed to avoid flooding by tides, yet in cover dense enough to be hidden from predators and to support the relatively large nest (Storey *et al*., 1988). Females lay approximately 4-8 eggs, which hatch in 18-27 days (U.S. Fish and Wildlife Service, 1985b). Both parents care for the young; while one forages, the other adult broods the chicks (U.S. Fish and Wildlife Service, 1985b). By the age of two days, chicks will accompany adults on foraging trips; however, adults have been observed feeding fully grown chicks of at least six weeks of age within 25 meters of their incubation nest (U.S. Fish and Wildlife Service, 1985b).

Very limited evidence exists for inter-marsh movements by rails, and this subspecies is resident in its home marsh except under unusual circumstances (Zembal, 1989). Within marsh movements are also confined and generally no greater than 400 meters (Zembal, 1989). Minimum home range sizes for nine rails that were studied using radio telemetry at Upper Newport Bay varied from approximately 0.3 to 1.7 hectares, with larger areas and daily movements by first year birds attempting to claim their first breeding territories (Zembal, 1989). Despite the lack of direct evidence for inter-marsh movement by rails, at least four sites where rails appeared to be extirpated for six or more years were subsequently re-occupied, indicating likely inter-marsh re-colonization (Zembal and Hoffman, 2001).

Historic and Current Range: The rail currently inhabits coastal marshes from the Carpinteria Marsh in Santa Barbara County, California, to Bahia de San Quintin, Baja California, Mexico (Zembal, 1989; Zembal *et al*., 1998). It is believed that most salt marshes along the coastline at one time supported clapper rails (Grinnell *et al*., 1918), but recent census data indicate that less than 50 percent of the coastal wetlands in California are currently occupied (Zembal *et al*., 1998).

Rangewide Trends and Current Threats: The first rail census in southern California was conducted in 1972-73, and the population was estimated at about 500 pairs (Wilbur, 1974). Annual surveys conducted from 1980 to 2001 showed an erratic trend in the population, with a peak estimate of 325 pairs in 1996 (Zembal and Hoffman, 2001). The most recent population census in 2001 found 217 pairs (Zembal and Hoffman, 2001). The three largest sub-populations

(at Newport Bay, Tijuana Estuary, and Seal Beach National Wildlife Refuge) comprised 86 percent of the breeding rails in southern California in 2001 (Zembal and Hoffman, 2001). Many smaller rail sub-populations are under threat of extirpation, but with appropriate management could become nuclei for recovery (U.S. Fish and Wildlife Service, 1985b). The number of marshes inhabited by breeding rails in coastal southern California has fluctuated widely since population censuses began in 1980. The number of occupied marshes declined from 19 marshes in 1984 to 8 in 1989, but increased to 16 occupied marshes in 1997 (Zembal *et al.*, 1998).

Habitat loss at several major estuaries in southern California approaches ninety-nine percent (U.S. Fish and Wildlife Service, 1985b). Although salt-marsh habitat loss, degradation, and fragmentation are the leading threats to rails, they are also threatened by disturbance, diseases, contaminants, and predation by non-native red foxes (Thelander and Crabtree, 1994). Rails may also be hit by vehicles in marshes adjacent to or bisected by roads (Zembal *et al.*, 1989).

Evaluation Results: As with the California clapper rail, two WVs were calculated for the light-footed clapper rail, based on UF_As of 1 or 3. However, due to the light-footed rail's smaller body weight, WVs are slightly less than those for the California rail. The UF_A of 1 resulted in a WV of 0.040 mg/kg, while the UF_A of 3 yielded a WV of 0.013 mg/kg.

Based on the light-footed rail's diet, which has a greater percentage of trophic level 3 organisms than in the California rail's diet, the trophic level concentrations expected under the Average Concentration TL Approach would produce a DC value of 0.053 mg/kg. This value is more than 400 percent of the lower WV (0.013 mg/kg). The Highest TL Approach produces a DC value of 0.024 mg/kg, 185 percent of the same WV. Both levels of WV exceedance demonstrate that, if 3 is the appropriate UF_A to determine a protective RfD and WV (0.013 mg/kg) for the light-footed clapper rail, the TRC under either TL approach is likely to result in dietary exposure that may place this subspecies at risk for adverse effects from methylmercury toxicity.

No information was found regarding diet-to-egg relationships for this subspecies, so no parallel assessment could be made regarding the appropriateness of 3 as the UF_A. Although it is reasonable to assume that both the light-footed and California clapper rails would be similarly sensitive to methylmercury, it is possible that the light-footed rail is better adapted to detoxify ingested methylmercury because of its more piscivorous diet (see Section III,D: Determination of Reference Dose). If so, then it may be more appropriate to consider the light-footed rail as an obligate piscivore, using the RfD and subsequent WV (0.040 mg/kg) generated with the UF_A of 1.

Comparison of the DC values expected from both TL approaches with the higher WV (0.040 mg/kg) produces variable results. The DC value from the Average Concentration TL Approach (0.053 mg/kg) is more than 130 percent of this WV, indicating dietary exposure is still likely to place these rails at risk of adverse effects from methylmercury toxicity. In contrast, the DC value from the Highest TL Approach (0.024 mg/kg) is only 60 percent of this higher WV, indicating a dietary exposure not likely to place light-footed rails at risk from the TRC.

Regardless of which UF_A (1 or 3) and subsequent WV (0.040 or 0.013) are used in the analysis, the trophic level concentrations expected under the Average Concentration TL Approach would result in a DC value substantially greater than either WV. Dietary exposure under this TL approach may place light-footed clapper rails at risk for adverse effects from methylmercury toxicity. However, comparison of the DC value expected from the Highest TL Approach with the two WVs results in conflicting conclusions. Assuming the UF_A of 1 is appropriate, the analysis suggests that applying the TRC under the Highest TL Approach would be sufficient to maintain dietary exposure at or below the corresponding protective WV (0.040 mg/kg). If the UF_A of 3 is the more appropriate value, then the TRC under this TL approach would result in a dietary exposure above the corresponding WV (0.013 mg/kg). Given the various uncertainties and assumptions used in these analyses (*e.g.*, dietary composition, food chain multipliers), the only conclusion that can be drawn at this point is that, of the two TL approaches evaluated, the Highest TL Approach poses less risk of a dietary exposure that could place light-footed clapper rails at risk for adverse effects from methylmercury toxicity. Further research must be conducted to verify whether the trophic level concentrations expected under the Highest TL Approach are sufficient or need to be lower to ensure adequate protection for the light-footed rail.

VIII.E. Yuma Clapper Rail

The Yuma clapper rail was federally listed as endangered on March 11, 1967 (32 Federal Register 4001). The Yuma Clapper Rail Recovery Plan, approved in 1983, provides background information on the species and identifies new or ongoing tasks necessary to achieve recovery of this species (U.S. Fish and Wildlife Service, 1983). The State of California added the bird to its list of rare wildlife in May of 1971 and later listed it as threatened on February 22, 1978.

Life History: Yuma clapper rail habitat is characterized by cattail (*Typha*), bulrush (*Scirpus*), or tule stands, and shallow, slow-moving water near high ground. Cattail and bulrush stands are often dissected by narrow channels of flowing water that may be covered by downed vegetation. These open channels are important for foraging. Rails commonly use areas with low stem densities and little residual vegetation. They are also found in the ecotone between emergent vegetation and higher ground, such as the shoreline, channel edge, or hummocks in a marsh. In studies conducted along the lower Colorado River, rails were found to use areas far from a vegetative edge during early winter (Conway *et al.*, 1993). The depth of water used by clapper rails also varied with season, with shallower water used during the breeding season, and water of moderate depth used during the winter. Although clapper rails are often found in larger stands of vegetation, they have also been found to use patches of habitat within agricultural drains (Bennett and Ohmart, 1978).

The Yuma clapper rail begins breeding activities in February, with egg-laying from March to July in marshes along the Colorado River from the Nevada/California border south to the Colorado River Delta region in Mexico. Chicks generally fledge by mid-September (Eddleman and Conway, 1994). It builds its nest on a raised platform of vegetation concealed in dense marsh vegetation (Patten *et al.*, in press). Males may build multiple nests, and the female chooses one

for egg-laying. Alternate nests are used as platforms for loafing, preening, and as brood platforms, but may also be useful for incubation if predators or high water disturb the primary nest (Eddleman and Conway, 1994). This subspecies is partially migratory, with many birds wintering in brackish marshes along the Gulf of California but some remain on their breeding grounds throughout the year (U.S. Bureau of Land Management, 2001). Yuma clapper rails are found around the Salton Sea, and in agricultural drains and canals that support marsh vegetation (i.e., cattail, giant bulrush, alkali bulrush, and common reed). This subspecies breeds only in the lower Colorado River Valley and in the Salton Sink, the latter area holding about 40 percent of the United States population (Setmire *et al*., 1990). The breeding site for the largest population of the Yuma clapper rail in the United States is at the Wister unit of the California Department of Fish and Game (CDFG) Imperial Wildlife Area, near the Salton Sea. The sea's elevation is important to the Yuma clapper rail (U.S. Department of the Interior, 1998) as clapper rails use shallow freshwater habitat that has formed at the mouths of many of the inflows to the Salton Sea. Yuma clapper rails avoid deeper water because it increases juvenile mortality (California Department of Fish and Game, 1990).

Historic and Current Range: The Yuma clapper rail occurs primarily in the lower Colorado River Valley in California, Arizona, and Mexico, and is a fairly common summer resident from Topock south to Yuma in the U.S. and at the Colorado River Delta in Mexico. There are also populations of this subspecies at the Salton Sea in California, and along the Gila and Salt Rivers to Picacho Reservoir and Blue Point in central Arizona (Rosenberg *et al*., 1991). In recent years, individual clapper rails have been heard at Laughlin Bay and Las Vegas Wash in southern Nevada (Nevada Division of Wildlife, 1998). Population centers for this subspecies include Imperial Wildlife Management Area (Wister Unit), Sonny Bono Salton Sea National Wildlife Refuge (NWR), Imperial NWR, Cibola NWR, Mittry Lake, West Pond, Bill Williams Delta, Topock Gorge, and Topock Marsh.

In California this species nests along the lower Colorado River, in wetlands along the Coachella Canal, the Imperial Valley, the upper end of the Salton Sea at the Whitewater River delta, and Salt Creek (NatureServe, 2001). Hydroelectric dams along the Colorado River have apparently increased the amount of marsh habitat, and population numbers of the Yuma clapper rail may have increased expanding the range northward in response to the increase in available habitat (U.S. Bureau of Land Management, 2001). Also, habitat was expanded through the creation of the Salton Sea in the early 1900s.

Rangewide Trends and Current Threats: The U.S. Fish and Wildlife Service (1983) estimated a total of 1,700 to 2,000 individuals throughout the range of the subspecies. Between 1990 and 1999, call counts conducted throughout the subspecies range in the U.S. have recorded 600 to 1,000 individuals. In 1985, Anderson and Ohmart (1985) estimated a population size of 750 birds along the Colorado River north of the international boundary. A substantial population of Yuma clapper rails exists in the Colorado River Delta in Mexico. Eddleman (1989) estimated that 450 to 970 rails inhabited this area in 1987. Piest and Campoy (1998) reported a total of 240 birds responding to taped calls in the Cienega de Santa Clara region of the Delta. These counts

are only estimates of the minimum number of birds present. The population is probably higher than these counts show, since up to 40 percent of the birds may not respond in call surveys (Piest and Campoy, 1998). Based on the call count surveys, the population of Yuma clapper rails in the U.S. appears stable (U.S. Fish and Wildlife Service, unpublished data). The range of the Yuma clapper rail has been expanding over the past 25 years, and the population may be increasing (Ohmart and Smith, 1973; Monson and Phillips, 1981; Rosenberg *et al*., 1991; McKernan and Braden, 1999). A recent genetic analysis showed that this subspecies is outbred; population numbers of the Yuma clapper rail have not become low enough to reduce genetic diversity (U.S. Bureau of Land Management, 2001).

The Yuma clapper rail apparently expanded its range in the early 1900's in response to changes in the vegetation along the Colorado River. Damming and associated changes in hydrology induced vegetation changes in some areas that favored rails. At the same time, damming and diversion of the Colorado River reduced the amount of water flowing into the Colorado River Delta, and reduced the availability of rail habitats in the Delta. Approximately two-thirds of the formerly extensive marshlands of the Delta disappeared following completion of Hoover Dam (Sykes, 1937).

Yuma clapper rail habitat has been further affected by channelization, fill, dredging projects, bank stabilization, and water management practices along the Colorado River. Rail habitat has also been adversely affected by the spread of salt cedar (*Tamarisk ramosissima*). Salt cedar consumes an unusually high amount of water, which results in reduced wetland areas for vegetation preferred by the rail.

Many of the currently occupied breeding sites in the United States are on State and Federal lands that are protected and managed for wildlife (U.S. Fish and Wildlife Service, 1983). However, adequate water supplies are needed to assure the long-term availability of this habitat. Wintering areas and needs are not well known and require further study before habitat preservation needs can be determined. Many of the Mexican breeding sites are located in the Rio Colorado Delta area and require adequate flows in the lower Colorado River for long-term use by Yuma clapper rails. The population of Yuma clapper rails at the Cienega de Santa Clara is threatened by the loss of the source of water that maintains the wetland habitat.
Other threats to the Yuma clapper rail include mosquito abatement activities, agricultural activities, development, and the displacement of native habitats by exotic vegetation (California Department of Fish and Game, 1991).

Evaluation Results: The two WVs (0.013 and 0.040 mg/kg) calculated for the Yuma clapper rail are the same as those used for the light-footed clapper rail. However, due to the Yuma rail's reliance on higher trophic level organisms for its diet, the DC values expected with each TL approach are substantially higher than those expected for either the light-footed or California clapper rails.

The WV for the Yuma rail calculated using the UF_A of 3 is 0.013 mg/kg. The DC value expected from trophic level concentrations under the Highest TL Approach is 0.057 mg/kg, more than 430 percent of the WV (see Table 7). The DC value from the Average Concentration TL Approach is 0.125 mg/kg, almost 1000 percent of the WV (see Table 5). Clearly, if 3 is the appropriate UF_A to determine a protective RfD and WV for the Yuma clapper rail, the TRC under either TL approach is likely to result in dietary exposure that may place this subspecies at risk for adverse effects from methylmercury toxicity.

The WV calculated using the UF_A of 1 is 0.040 mg/kg. This WV (0.040 mg/kg) is substantially closer than the previous WV to the DC value of 0.125 mg/kg expected from the Average Concentration TL Approach, but this DC is still more than 300 percent of this higher WV (see Table 5). This higher WV is even closer to the DC value of 0.057 mg/kg expected from the Highest TL Approach (see Table 7); however, a DC value exceeding the WV by more than 40 percent is still likely to result in a dietary exposure that may place Yuma rails at risk for adverse effects from methylmercury toxicity. Based on these comparisons, both TL approaches would still be insufficient to maintain dietary exposure in this subspecies at or below the calculated WVs.

VIII.F. Western Snowy Plover

The Pacific coast population of the western snowy plover was federally listed as threatened on March 5, 1993 (58 Federal Register 12864) and critical habitat was designated on December 7, 1999 (64 Federal Register 68508). A draft recovery plan for the species has been completed (U.S. Fish and Wildlife Service, 2001).

Life History: Western snowy plovers prefer coastal beaches that are relatively free from human disturbance and predation. Sand spits, dune-backed beaches, beaches at creek and river mouths, and salt pans at lagoons and estuaries are the preferred habitats for nesting. The attributes considered essential to the conservation of the coastal population of the western snowy plover can be found in the final ruling for the designation of critical habitat (64 Federal Register 68508). The primary constituent elements for the western snowy plover are those habitat components that are essential for the primary biological needs of foraging, nesting, rearing of young, roosting, and dispersal, or the capacity to develop those habitat components. The primary constituent elements of critical habitat for the species are provided by intertidal beaches (between mean low water and mean high tide), associated dune systems, and river estuaries. Important components of the beach/dune/estuarine ecosystem include surf-cast kelp, sparsely vegetated foredunes, interdunal flats, spits, washover areas, blowouts, intertidal flats, salt flats, and flat rocky outcrops. Several of these components (sparse vegetation, salt flats) are mimicked in artificial habitat types used less commonly by western snowy plovers (*i.e.*, dredge spoil sites and salt ponds and adjoining levees).

The breeding season for westem snowy plovers extends from March to late September, with birds at more southerly locations breeding earlier. Most nesting occurs on unvegetated or

moderately vegetated, dune-backed beaches and sand spits. Other less common nesting habitats include salt pans, dredge spoils, and salt pond levees. Nest site fidelity is common, and mated birds from the previous breeding season frequently reunite. Nest sites are scrapes in the substrate, in which females lay eggs (typically three but up to six). Both sexes incubate eggs, with the female tending to incubate during the day and the male at night (Warriner *et al*., 1986). Snowy plovers often renest if eggs are lost. Hatching lasts from early April through mid-August, with chicks fledging approximately one month after hatching. Adult plovers tend chicks while feeding, often using distraction displays to lure predators and people away from chicks. Females generally desert both mates and broods by the sixth day after hatching, and thereafter the chicks are typically accompanied by only the male. While males rear broods, females obtain new mates and initiate new nests (Page *et al*., 1995)

Historic and Current Range: The Pacific coast population of the western snowy plover breeds primarily on coastal beaches from southern Washington to southern Baja California, Mexico. Historically, western snowy plovers bred or wintered at 157 locations on the Pacific coast, including 133 sites in California. Larger numbers of birds are found in southern and central California, in Monterey Bay (estimated 200 to 250 breeding adults), Morro Bay (estimated 85 to 93 breeding adults), Pismo Beach to Point Sal (estimated 130 to 246 breeding adults), Vandenberg Air Force Base (estimated 130 to 240 breeding adults), and the Oxnard Lowland (estimated 69 to105 breeding adults).

During the non-breeding season western snowy plovers may remain at breeding sites or may migrate to other locations. Most winter south of Bodega Bay, California. Many birds from the interior population winter on the central and southern coast of California.

Rangewide Trends and Current Threats: Historical records indicate that nesting western snowy plovers were once more widely distributed in coastal Washington, Oregon and California than they are currently. Only 1,200 to 1,900 adult western snowy plovers remain on the Pacific coast of the United States (Page *et al*., 1991). In 1995, approximately 1,000 western snowy plovers occurred in coastal California. Historically, western snowy plovers bred at 53 coastal locations in California prior to 1970. Only eight sites continue to support 78 percent of the remaining California coastal breeding population. These are San Francisco Bay, Monterey Bay, Morro Bay, the Callendar-Mussel Rock dunes area, the Point Sal to Point Conception area (Vandenberg Air Force Base), the Oxnard lowland, Santa Rosa Island, and San Nicolas Island (Page *et al*., 1991).

The Pacific coast population of the western snowy plover has experienced widespread loss of nesting habitat and reduced reproductive success at many nesting locations due to urban development and the encroachment of European beachgrass (*Ammophila arenaria*). Human activities such as walking, jogging, unleashed pets, horseback riding, and off-road vehicles can destroy the western snowy plover's cryptic nests and chicks. These activities can also hinder foraging behavior, cause separation of adults and their chicks, and flush adults off nests and away from chicks, thereby interfering with essential incubation and chick-rearing behaviors. Predation by coyotes, foxes, skunks, ravens, gulls, and raptors has been identified as a major factor limiting

western snowy plover reproductive success at many Pacific coast sites.

Evaluation Results: Compared to the other species considered in this evaluation, the western snowy plover is unique in that little of its overall diet is comprised of aquatic organisms. Although the species lives and nests along coastal and estuarine river beaches, the scientific literature indicates that the bulk of the plover diet comes from larval and adult terrestrial insects (primarily flies and beetles). Due to this dietary characteristic, all the analyses performed in this effort indicate that the TRC should not result in a dietary exposure that would place snowy plovers at risk for adverse effects from methylmercury toxicity (see Tables 5 & 7). Dietary concentration values expected from both of the TL approaches should remain substantially below the plover's calculated WV (0.026 mg/kg). Even when using the alternative reference dose (RfD) generated with the interspecies uncertainty factor (UF_A) of 3, expected DC values remain well below the corresponding lower WV (0.009 mg/kg).

These results must be interpreted with some caution, however, as recent research suggests plovers may be at risk from a unique dietary methylmercury exposure pathway not previously considered in toxicity assessments. Hothem and Powell (2000) collected 68 abandoned or inviable snowy plover eggs from five sites in southern California between 1994 and 1996. Twenty-three of these eggs were analyzed for metals and trace elements. Total mean mercury concentrations in these eggs ranged from 0.078 to 0.19 mg/kg. These values are substantially below accepted lowest observed adverse effects concentrations (LOAEC) for avian eggs, and the authors concluded that concentrations of mercury and other environmental contaminants were not sufficiently elevated in the study eggs to be contributing to population declines. However, snowy plover eggs collected in 2000 from Point Reyes National Seashore in northern California revealed highly elevated mercury concentrations (U.S. Fish and Wildlife Service, unpublished data). Nine failed-to-hatch eggs and two abandoned eggs were collected and analyzed for total mercury. Dry weight concentrations ranged from 0.9 to 12.48 mg/kg, with a mean of 2.56 mg/kg. Adjusted for percent moisture at the time of analysis and moisture loss from the time of laying, the mean fresh wet weight (fww) concentration in the failed and abandoned eggs was reported as 1.07 and 0.27 mg/kg, respectively, with a mean of 0.92 mg/kg for all 11 eggs. The maximum concentration detected from the failed eggs (12.48 mg/kg dry weight) adjusted to 3.1 mg/kg fww. This value is nearly as high as the highest concentration yet detected (3.3 mg/kg fww) in eggs of Fortser's terns, an exclusively piscivorous species, collected from the south San Francisco Bay area (Schwarzbach and Adelsbach, 2002). Mean and maximum concentrations in the failed eggs were substantially above accepted avian egg LOAECs [0.5 mg/kg (Fimreite, 1971); ~0.8 mg/kg (Heinz, 1979)], possibly high enough to account for egg failure through direct toxic effects to plover embryos.

The U.S. Fish and Wildlife Service investigators observed an order of magnitude variation in egg mercury concentrations between the different nests sampled along Point Reyes National Seashore in 2000, with no apparent spatial gradients. As mercury in eggs is thought to closely reflect recent dietary uptake (Walsh, 1990), the Point Reyes data indicated to the investigators that the degree of variation observed reflected a highly heterogenous source of dietary mercury. There

are no known mercury inputs to the coastal beaches used by breeding plovers; however, the investigators noted that an inoperative mercury mine continues to discharge mercury-laden sediments into Tomales Bay, east of the Point Reyes peninsula. Although breeding plovers likely do not forage in Tomales Bay, the investigators suggested that marine mammals foraging in this water body may serve as a mercury pathway into the plover diet. Marine pinnipeds are known to accumulate mercury, usually exhibiting the highest reported tissue concentrations among non-human mammals (Eisler, 2000). As snowy plovers are known to feed on insect larvae that develop on marine mammal carcasses (Page *et al.*, 1995), the Point Reyes investigators hypothesized that the elevated plover egg mercury concentrations they observed were the result of localized consumption of invertebrates from pinniped carcasses washed ashore into plover breeding territories. This hypothesis is supported by the fact that at least four marine pinnipeds washed ashore at Point Reyes National Seashore during the 2000 plover breeding season, including a harbor seal carcass that was allowed to decompose on site near the plover nest with the maximum observed egg mercury concentration (Ruhlen and Abbott, 2000).

More work is needed to confirm whether plovers may be exposed to mercury via marine mammal carcasses, and it is not currently possible to incorporate this potential exposure pathway into the methodology developed for this evaluation. To do so would require an analysis of mercury biomagnification from pinniped prey items into the insect larvae developing on pinniped carcasses, information currently unavailable. Even if the hypothesis is confirmed, the mercury levels in Tomales Bay prey biota may already be substantially elevated above the trophic level concentrations expected under the human health TRC, due to the historic and ongoing mercury inputs from the upstream mine. As noted above, the analyses performed for this effort indicate that dietary exposure in snowy plovers should not place them at risk from methylmercury toxicity by either of the TL approaches described. However, given the uncertainties surrounding the potential marine mammal pathway and the plover's sensitive conservation status, applying the Highest TL approach to the TRC would provide the most reasonable assurance of protection.

VIII.G. Bald Eagle

The bald eagle was listed as federally endangered in 1978 (43 Federal Register 6230). The Pacific Bald Eagle Recovery Plan was released in 1986 for the recovery and maintenance of bald eagle populations in the 7-state Pacific recovery region (Idaho, Nevada, California, Oregon, Washington, Montana, and Wyoming) (U.S. Fish and Wildlife Service, 1986). In recent years, the status of bald eagle populations has improved throughout the United States. The bald eagle was downlisted from endangered to threatened on July 12, 1995, throughout the lower 48 states (60 Federal Register 36000). A proposed rule to remove the species from the list of endangered and threatened wildlife was made on July 6, 1999 (64 Federal Register 36454) but this rule has not been finalized. Critical habitat has not been designated for this species. In addition to the Endangered Species Act, the bald eagle is protected under the Migratory Bird Treaty Act of 1918, as amended (16 U.S.C. §§703-712) and the Bald Eagle Protection Act of 1940, as amended (16 U.S.C. §§668-668d).

Life History: The species is long-lived, and individuals do not reach sexual maturity until four or five years of age. Breeding generally occurs February to July (Zeiner *et al*., 1990) but breeding can be initiated as early as January via courtship, pair bonding, and territory establishment. The breeding season normally ends approximately August 31 when the fledglings have begun to disperse from the immediate nest site. One to three eggs are laid in a stick platform nest 50 to 200 feet above the ground and usually below the tree crown (Zeiner *et al*., 1990). Incubation may begin in late February to mid-March, with the nestling period extending to as late as the end of June. From June thru August, the chicks remain restricted to the nest until they are able to move around within their environment.

Nesting territories are normally associated with lakes, reservoirs, rivers, or large streams and are usually within two miles from water bodies that support an adequate food supply (Lehman, 1979; U.S. Fish and Wildlife Service, 1986). Most nesting territories in Califomia occur from 1000 to 6000 feet elevation, but nesting can occur from near sea level to over 7000 feet (Jurek, 1988). The majority of nests in California are located in ponderosa pine and mixed-conifer stands and nest trees are most often ponderosa pine (*Pinus ponderosa*) (Jurek, 1988). Other site characteristics, such as relative tree height, tree diameter, species, position on the surrounding topography, distance from water, and distance from disturbance, also appear to influence nest site selection (Lehman *et al*., 1980; Anthony and Isaacs, 1981). Bald eagles often construct up to five nests within a territory and alternate between them from year to year (U.S. Fish and Wildlife Service, 1986). Nests are often reused and eagles will add new material to a nest each year (DeGraaf *et al*., 1991). Lehman (1979) found that 73 percent of nest sites surveyed were within one-half mile of a waterbody, 87 percent within 1 mile, and 100 percent within 2 miles.

Isolation from disturbances is an important feature of bald eagle wintering habitat. Wintering habitat is associated with open bodies of water, with some of the largest wintering bald eagle populations in the Klamath Basin (Detrich, 1981, 1982). Smaller concentrations of wintering birds are found at most of the larger lakes and man-made reservoirs in the mountainous interior of the northern half of the state and at scattered reservoirs in central and southwestern California. Some of California's breeding birds winter near their nesting territories.

Historic and Current Range: The bald eagle once nested throughout much of North America near coasts, rivers, lakes, and wetlands. The species experienced population declines throughout most of its range, including California, due to exposure to environmental contaminants, habitat loss and degradation, shooting, and other disturbances (Detrich, 1981; Stalmaster *et al*., 1985; U.S. Fish and Wildlife Service, 1986). The species' status has improved since the initial listing under the Endangered Species Act.

The bald eagle continues to be found throughout much of North America and breeds or winters throughout California, except in the desert areas (Zeiner *et al*., 1990; DeGraaf *et al*., 1991). In California, most breeding occurs in Butte, Lake, Lassen, Modoc, Plumas, Shasta, Siskiyou, and Trinity Counties (Zeiner *et al*., 1990). California's breeding population is resident year-long in most areas as the climate is relatively mild (Jurek, 1988). Between mid-October and December,

migratory bald eagles arrive in California from areas north and northeast of the state. The wintering populations remain in California through March or early April.

Rangewide Trends and Current Threats: Though the construction of dams has limited the range of anadromous fish, an important historic bald eagle prey base, reservoir construction and the stocking of fish in reservoirs in the west have provided bald eagles with habitat for population expansion (Detrich, 1981; U.S. Fish and Wildlife Service, 1986). The Califomia bald eagle nesting population has increased in recent years from under 30 occupied territories in 1977 to 151 occupied territories in 1999 (Jurek, 2000). Based upon annual wintering and breeding bird survey data, it is estimated that between 100-300 bald eagles winter on National Forests in the Sierra Nevada, and at least 151-180 pairs remain year-round to breed (U.S. Forest Service, 2000). Most of the breeding population is found in the northern third of the state, primarily on public lands. Seventy percent of nests surveyed in 1979 were located near reservoirs (Lehman, 1979) and this trend has continued, with population increases occurring at several reservoirs since the time of that study.

The Bald Eagle Recovery Plan identifies reasons for the decline of the bald eagle, and states that habitat loss is the most important long-term threat to bald eagle populations. Other threats to the bald eagle include recreational development and human activities affecting the suitability of breeding, wintering, and foraging areas. Bald eagles are susceptible to disturbance by human activity during the breeding season, especially during egg laying and incubation, and such disturbances can lead to nest desertion or disruption of breeding attempts (U.S. Fish and Wildlife Service, 1986). Types of disturbance include recreational activities, fluctuating fish populations and availability of roost trees as a result of reservoir level fluctuations, wild fire, fragmentation of habitat, home sites, campgrounds, mines, timber harvest, and roads. Human activities are more likely to disturb bald eagles when located near roosting, foraging, and nesting areas (Stalmaster and Kaiser, 1998; Stalmaster *et al*., 1985; U.S. Fish and Wildlife Service, 1986).

Evaluation Results: For this effort, a weighted risk approach was taken to determine the appropriate eagle diet for calculation of wildlife values, based on the highest trophic level composition reasonably likely to occur, from the predominant habitat type characteristic of California's breeding bald eagles. In effect, this diet represented the greatest potential for dietary methylmercury exposure in bald eagles. Although alternate diets with higher trophic level compositions could be hypothesized, the diet for this effort was determined using a robust dataset for breeding California eagles.

Results of the analyses performed indicate that applying the human health TRC under the Average Concentration TL Approach is likely to result in dietary exposure that may place bald eagles at risk for adverse effects from methylmercury toxicity. The eagle's dietary concentration (DC) of methylmercury expected from the trophic level concentrations under this approach would be more than 230 percent of the eagle's calculated WV (DC - 0.431 mg/kg, WV - 0.184 mg/kg) (see Table 5). While the extent of any potential adverse effects from this DC cannot be quantified, the degree of WV exceedance suggests a high probability that dietary methylmercury

exposure from the TRC could reach a level at which adverse effects to bald eagles may be expected.

In contrast, the DC expected from the concentrations under the Highest TL Approach (DC - 0.196 mg/kg) would be less than 10 percent above the eagle's WV (see Table 7). Given the small differential between the two values, and a recognition of the various uncertainties and assumptions (*e.g.*, LOAEL-to-NOAEL extrapolation, allometric-derived FIR) inherent in the methodology, it is reasonable to conclude that dietary exposure resulting from applying the TRC under the Highest TL Approach should not place bald eagles at risk for adverse effects from methylmercury toxicity.

IX. EVALUATION RESULTS SUMMARY

IX.A. Average Concentration Trophic Level Approach

Based on the analyses conducted for this evaluation, applying the TRC with the estimated trophic level methylmercury concentrations under the Average Concentration TL Approach may be sufficiently protective for only two of the seven species considered: southern sea otter and Western snowy plover. The five other species examined (California least tern; California, light-footed, and Yuma clapper rails; bald eagle) would likely have dietary exposures under this approach that may place them at risk for adverse effects from methylmercury toxicity. The California clapper rail would not have been considered at risk under this approach if the WV generated with the UF_A of 1 was appropriate to represent the rail's sensitivity to methylmercury toxicity, relative to mallard ducks. However, the parallel evaluation discussed previously demonstrated that the WV generated with the UF_A of 3 was more appropriate for this subspecies, resulting in the conclusion that California clapper rails would also likely have dietary exposures that may place them at risk under this TL approach.

IX.B. Highest Trophic Level Approach

This approach, with its lower estimated trophic level methylmercury concentrations, would provide a greater degree of protection than the prior alternative. Applying the TRC under the Highest TL Approach should be sufficiently protective for four of the seven species considered: southern sea otter, California clapper rail, Western snowy plover, and bald eagle. At this time, no conclusion can be drawn regarding the light-footed clapper rail. If this subspecies' sensitivity to methylmercury is the same as the California clapper rail (*i.e.*, the alternative WV generated with the UF_A of 3 is appropriate), and the analysis of its dietary composition is correct, the light-footed rail would likely have dietary exposures under this approach that may place them at risk. However, if other biological characteristics (*e.g.*, a greater ability to detoxify ingested methylmercury, lower diet-to-egg transfer efficiency) indicate the WV generated with the UF_A of 1 is more appropriate for the light-footed rail, the evaluation results suggest this TL approach should be sufficiently protective for this subspecies. Further research is required to definitively answer these questions. The evaluation for the Yuma clapper rail, regardless of the WV used in

the analysis, indicates this subspecies would likely have a dietary exposure under this approach that may place it at risk for adverse effects from methylmercury toxicity. The same questions surrounding relative sensitivity apply to this subspecies, and research should be initiated to answer these questions and determine appropriate trophic level methylmercury concentrations to provide sufficient protection against toxicity. Finally, although methylmercury concentrations for all three trophic levels are expected to be substantially lower under this approach, the estimated trophic level 3 concentration of 0.075 mg/kg would still not be low enough to remove the potential risk of adverse effects from dietary methylmercury exposure for the California least tern. Because of the tern's small body size and its diet of exclusively trophic level 3 fish, this species may be at an elevated risk from methylmercury toxicity.

X. CONSIDERATION OF OTHER TAXONOMIC GROUPS

As explained previously in this document, the evaluation of the TRC's potential to adversely affect federally listed species in California was conducted with the assumption that upper trophic level wildlife species (*i.e.*, piscivorous or omnivorous birds and mammals) would have the greatest inherent risk from methylmercury exposure, due to methylmercury's propensity to bioaccumulate and biomagnify as it moves upward through aquatic food chains. However, there are numerous other listed species in California to consider (see Appendix) which may be adversely affected by the methylmercury TRC. Once the TRC's protectiveness was evaluated for the upper trophic level birds and mammals, the scientific literature was reviewed to assess whether the methylmercury concentrations expected under each TL approach may be protective for the remaining taxonomic groups.

X.A. Fish

The methodology employed for birds and mammals in this effort was based on an assessment of potential toxicity through ingestion of methylmercury-contaminated fish, shellfish, and other aquatic organisms. For fish, assessment of risk from the TRC was based solely on the potential for adverse effects associated with the tissue methylmercury concentrations expected under each of the TL approaches. It should be noted, however, that muscle tissue-bound concentrations represent the amount of methylmercury sequestered from dietary input over a fish's lifetime. It is possible that levels of circulatory methylmercury, reflective of current dietary exposure, may be responsible for any adverse effects. This possibility is due to the fact that re-mobilization of muscle-bound methylmercury may be negligible unless a reduction in available food necessitates catabolic utilization of muscle-bound proteins. However, until further work on circulatory methylmercury is conducted, muscle tissue concentrations remain the most appropriate indicator for evaluating the impact of the TRC on fish.

A great deal of research has been conducted over the years on the bioaccumulation of mercury by fish, providing data on fish tissue mercury concentrations associated with both overt and subtle toxicological effects (see reviews by: Wiener and Spry, 1996; Jarvinen and Ankley, 1999; Eisler,

2000; Wiener *et al*., 2002). Both Wiener *et al*. (2002) and Eisler (2000) examined the relationships between body burden and toxicological significance in several fish species. All of the overt effects concentrations presented were approximately an order of magnitude above even the highest concentration expected in trophic level 4 fish (0.66 mg/kg) when applying the TRC under the Average Concentration TL Approach.

Wiener *et al*. (2002) stated that, because of the high neurotoxicity of methylmercury, exposure levels causing more subtle adverse behavioral effects are likely much lower than those that would result in overt toxicity. These sublethal neurotoxic effects can impair the ability of fish to locate, capture, and ingest prey and to avoid predators. Unfortunately, studies that demonstrate these effects are generally based on waterborne concentrations of mercury, with few providing data on subsequent fish tissue levels.

Fjeld *et al*. (1998) demonstrated long-term impairment in feeding behavior of grayling (*Thymallus thymallus*) that had been exposed as eggs to waterborne methylmercuric chloride. The 3 year old grayling that exhibited impairment developed from yolk-fry with mercury concentrations as low as 0.27 mg/kg. The yolk-fry concentration of 0.27 mg/kg resulted from eggs in the treatment group exposed to 0.8 ug/L methylmercuric chloride, much higher than environmentally realistic waterborne levels. Compared to the control group, 3 year old fish from the 0.8 ug/L treatment group exhibited a 15 percent reduction in feeding efficiency and a 49 percent reduction in competitive feeding ability.

Based on limited data indicating that mercury concentrations in embryos of methylmercury-exposed brook trout are approximately 20 percent of that in the maternal axial muscle tissue, Fjeld *et al*. (1998) calculated that their lowest observed adverse effects concentration (LOAEC) for grayling yolk-fry (0.27 mg/kg) would translate to a maternal muscle tissue concentration of 1.35 mg/kg. This is double the concentration expected in trophic level 4 fish (0.66 mg/kg) under the Average Concentration TL Approach. Extrapolating a matemal muscle methylmercury concentration from a waterborne-induced embryolarval concentration is tenuous for two reasons: the outermost membrane of fish eggs may retard the uptake of both inorganic and methylmercury from the water column, and maternally-derived egg concentrations may be more associated with dietary intake during egg formation rather than existing muscle-bound concentrations (Latif *et al*, 2001; Hammerschmidt *et al*., 1999). However, Hammerschmidt *et al*. (1999) sampled wild yellow perch (*Perca flavescens*) from four seepage lakes in northern Wisconsin and found that the concentration of total mercury in eggs ranged from 20 to 5 percent of the concentration in the maternal carcass. Using this range of concentration ratios, the embryolarval LOAEC of 0.27 mg/kg could translate to maternal muscle tissue concentrations from 1.35 mg/kg (5:1 adult-egg ratio) to 5.4 mg/kg (20:1 adult-egg ratio).

These data suggest that the adult fish tissue concentrations expected under either trophic level approach would result in egg and embryolarval concentrations substantially below the LOAEC (0.27 mg/kg) reported for grayling. How far below the LOAEC depends on the trophic level approach used and assumptions regarding the adult-egg concentration ratio. By using

conservative assumptions (*i.e.*, 5:1 adult-egg ratio), the tissue concentration expected for trophic level 4 fish (0.66 mg/kg) under the Average Concentration Trophic Level Approach would result in an egg concentration of 0.132 mg/kg, approximately half the grayling LOAEC. Applying the same adult-egg concentration ratio to the tissue concentration expected for trophic level 4 fish (0.3 mg/kg) under the Highest Trophic Level Approach would result in an egg concentration of 0.06 mg/kg, approximately one-fifth the grayling LOAEC. While Fjeld *et al*. (1998) made no conclusions regarding a NOAEC (no observed adverse effects concentration) in their experiment, they did not observe any feeding behavior impairment in their lowest dose treatment group. This treatment group was exposed to a waterborne methylmercury concentration of 0.16 ug/L, and the resulting yolk-fry had a mercury concentration of 0.09 mg/kg wet weight. Although it can be determined with some certainty that the egg mercury concentration (0.06 mg/kg) estimated from the trophic level 4 fish concentration under the Highest Trophic Level Approach would not result in feeding behavior impairments in grayling, the same cannot be said for the egg mercury concentration (0.132 mg/kg) estimated with the Average Concentration Trophic Level Approach. The relative magnitude of effects seen at the 0.27 mg/kg LOAEC for grayling yolk-fry (*i.e.*, 49% reduction in competitive feeding ability) suggests the potential for adverse effects may not be completely removed even when eggs have mercury concentrations around 0.132 mg/kg.

In a more recent study, Webber and Haines (2003) examined the potential for behavioral alterations in fish with environmentally realistic tissue methylmercury concentrations. They concluded that alterations in predator-avoidance behaviors in golden shiners (*Notemigonus crysoleucas*) with environmentally realistic tissue methylmercury concentrations (0.536 mg/kg) may increase vulnerability to predation. Golden shiners should be considered trophic level 3 fish, due to their natural diet of zooplankton and aquatic insects (Moyle, 2002). The effects concentration of 0.536 mg/kg is well above the concentrations expected for trophic level 3 fish under either of the TL approaches evaluated here (0.165 mg/kg - Average Concentration Trophic Level Approach; 0.075 mg/kg - Highest Trophic Level Approach). These data suggest that alterations in predator-avoidance behaviors would not be expected in trophic level 3 fish if the TRC is applied under either approach. Although these data do not allow for any definitive conclusions regarding adult trophic level 4 fish, the possibility that a tissue concentration of 0.536 mg/kg could result in adverse behavioral effects suggests that the more conservative trophic level concentrations expected from the Highest Trophic Level Approach may be warranted in order to ensure adequate protection for federally listed fish species.

In addition to the potential for sublethal neurotoxic effects, Wiener and Spry (1996) concluded that reduced reproductive success in wild fish populations is the most plausible adverse effect expected from environmentally realistic concentrations. They noted that methylmercury can impair reproduction by affecting gonadal development or spawning success in adult fish, or by reducing egg hatching success and embryolarval health and survival. Mercury concentrations affecting both hatching success and embryolarval health are directly linked to the adult female body burden (circulatory and/or muscle-bound concentrations), as the majority of mercury in developing eggs is methylmercury derived through maternal transfer (Wiener *et al*., 2002). However, only a small fraction of the total muscle-bound methylmercury is transferred to the egg

mass and eliminated during spawning (Wiener *et al*., 2002; Hammerschmidt *et al*., 1999). Several key studies on mercury and reproductive endpoints are discussed below.

Birge *et al*. (1979) describe the results of two experiments involving embryolarval stage rainbow trout (*Salmo gairdneri*) exposed to waterborne inorganic mercury. In one study, trout eggs exposed to approximately 100 ng/L exhibited reduced survival after four days, with 100 percent mortality after eight days (at approximately 200 - 300 ng/L). After days four and seven of the experiment, mercury content of the eggs was approximately 0.068 and 0.097 mg/kg, respectively. In a second study, trout eggs were placed in aquaria with mercury-enriched sediment and clean water. There was a 28 percent reduction in hatching success and a 49 percent reduction in 10-day survival with a sediment mercury concentration of approximately 1.05 mg/kg. In this treatment group, mercury in the water column was approximately 150 ng/L, and tissues from the hatched larvae contained approximately 0.041 mg/kg.

Both of the above experiments demonstrated substantial adverse effects at low embryolarval inorganic mercury concentrations. If the adult-egg concentration ratios from the previous discussion on grayling (Fjeld *et al*., 1998) were applied to these inorganic mercury concentrations in embryolarval rainbow trout (*e.g.*, 0.04 mg/kg larval concentration and 5:1 adult-egg ratio), adult muscle tissue concentrations as low as 0.2 mg/kg could be associated with severe reproductive effects. However, the adult-egg ratios are based on maternal transfer of accumulated mercury, which is predominantly methylmercury in both the adult tissue and the developing eggs (Wiener *et al*., 2002). The mechanisms of mercury bioaccumulation and maternal transfer prevent a reliable extrapolation of adult fish tissue methylmercury concentrations from concentrations of inorganic mercury in eggs or larvae. In addition, the waterborne concentrations of inorganic mercury (100 - 150 ng/L) used to achieve the observed effects concentrations in embryolarval rainbow trout are substantially above all but the most highly polluted natural waters (Wiener and Spry, 1996). These high waterborne concentrations necessary to see adverse effects in eggs may be due to the apparent ability of the outermost membrane on fertilized fish eggs to retard the uptake of both inorganic and methylmercury from the surrounding water column into the developing embryo (Hammerschmidt *et al*., 1999). In order to accurately assess adult fish muscle tissue levels associated with embryolarval effects, the effects should be related to matemally-derived methylmercury concentrations.

Matta *et al*. (2001) examined the effects of dietary methylmercury on reproduction and survival in three generations of mummichogs (*Fundulus heteroclitus*). Treatment groups were fed methylmercuric chloride-contaminated fish food until four target tissue concentrations were reached (0.2, 0.5, 1.0, and 11.0 mg/kg). Although adverse reproductive effects were observed in this study, they were only manifested in F_1 generation offspring of the treatment group containing tissue methylmercury concentrations of 11 and 12 mg/kg in males and females, respectively. These values are substantially higher than any of the trophic level concentrations expected with the TRC. Of greater importance from this study are the data indicating a significant increase in male mortality in the 0.5 mg/kg tissue concentration treatment group. Survival was somewhat reduced in the 0.2 mg/kg treatment group, but not significantly. However, the almost 50 percent

reduction in the 0.5 mg/kg group indicates significant mortality may occur at concentrations between 0.2 and 0.5 mg/kg. The mummichog is a trophic level 3 fish from the eastern seaboard, similar to the California killifish (*Fundulus parvipinnis*). Although the tissue concentrations associated with increased male mortality from this study (0.2 - 0.5 mg/kg) are considerably higher than the TL3 concentration (0.075 mg/kg) expected by applying the TRC under the Highest Trophic Level Approach, they are close to the TL3 concentration (0.165 mg/kg) expected under the Average Concentration Trophic Level Approach.

The influence of mercury exposure on more subtle reproductive parameters in natural settings was examined by Friedmann *et al*. (1996a). Two indices of gonadal function, gonadosomatic index (GSI) and gonadal sex steroid levels, were measured in northern pike (*Esox lucius*) collected from Lake Champlain, New York and Vermont, in 1994. Northern pike were selected because they are trophic level 4 fish, with a greater degree of mercury bioaccumulation than lower trophic level fish. The GSI was determined by the ratio of gonadal weight to total body weight. The mean total mercury concentration in muscle from the 14 fish sampled was 0.325 mg/kg (range: 0.117 - 0.623 mg/kg). The means for males (n = 7) and females (n = 7) were 0.347 and 0.303 mg/kg, respectively. The researchers found no significant correlation between mercury content, GSI, and gonadal sex steroids, suggesting that mercury exposure in natural settings might not exert as dramatic an effect on teleost fish reproduction as indicated by earlier laboratory findings. However, the researchers raised the possibility that the mercury levels they observed might have a more subtle influence on reproductive physiology which could be detected given a larger sample size.

To evaluate this possibility, the same researchers (Friedmann *et al*., 1996b) conducted a dietary methylmercury feeding experiment with juvenile walleye (*Stizstedion vitreum*). After six months of dietary exposure, fish in the low- and high-mercury diet groups had mean total mercury tissue concentrations of 0.254 and 2.37 mg/kg, respectively. The results for the low-mercury diet group are most relevant to this TRC analysis, as the mercury concentration in the test fish (0.254 mg/kg) is of the same magnitude as the concentrations expected in trophic level 4 fish under either trophic level approach. No significant differences from controls were seen in this low-mercury group for growth and mortality rates. The mean GSIs of male and female fish from both dietary groups were lower than in fish from the control group, but the differences were not statistically significant in the analysis of variance (ANOVA). However, when combining data from the two dietary groups, the mean GSI of male fish fed either mercury-contaminated diet was significantly lower than in males fed the control diet. Also, male fish in both groups exhibited varying degrees of testicular atrophy, greater in the high-mercury group. Mean GSIs for female fish in either treatment group were not significantly different from controls. Levels of plasma cortisol, which is important for stress response and immune function in teleost fish, were significantly lower in low-mercury fish than in control group fish. The above findings suggested to the authors that methylmercury at environmentally realistic fish tissue levels (0.254 mg/kg) may adversely affect reproductive success by impairing testicular development in young teleost fish and may reduce juvenile survival by impairing immune function.

However, in another study examining growth and reproductive endpoints in wild populations of mercury-contaminated fish, Friedmann *et al*. (2002) presented conflicting conclusions. Fifty-two male largemouth bass (*Micropterus salmoides*) were collected from three New Jersey water bodies of varying mercury contamination. Mean total mercury concentrations in muscle tissue were 0.30 mg/kg (Assunpink Lake), 1.23 mg/kg (Manasquan Reservoir), and 5.42 mg/kg (Atlantic City Reservoir). No significant differences between the three lakes were found for body weight, length, condition factor, or GSI. Also, no significant relationship was found between muscle mercury content and adrenocortical function, indicated by interrenal nuclear diameter and serum cortisol levels following stress. Liver somatic index (LSI) was significantly lower in fish from the Atlantic City Reservoir compared to the other two lakes, but this reduction could not be definitively correlated with mercury concentrations. The elevated mercury levels in fish from the Atlantic City Reservoir may have altered androgen profiles, as evidenced by greater levels of serum 11-ketotestosterone, but no cause-effect relationship could be established. Based on the above findings, the authors concluded that elevated mercury levels in fish (*i.e.*, as high as 5.42 mg/kg) do not substantially decrease indicators of general and reproductive health (*i.e.*, GSI). This finding is in contrast to the previous dietary mercury study with juvenile walleye which indicated that an even lower muscle concentration (2.37 mg/kg) was associated with impaired gonadal development (Friedmann *et al*., 1996b). As an explanation for this apparent discrepancy, Friedmann *et al*. (2002) pointed to findings that wild fish populations exposed to toxicants in their environment can develop adaptations that allow them to live in more polluted sites than are predicted with laboratory models. In further support of this explanation, the authors cite the observation by Friedmann *et al*. (1996a) that a correlation between muscle mercury content and reduced GSI did not exist in Lake Champlain northern pike.

Latif *et al*. (2001) collected female walleye during two successive spawning seasons from one mercury-contaminated lake and two relatively pristine lakes in Canada. Mean total mercury concentrations in muscle tissue, in mg/kg, were 0.182 (Lake Winnipeg), 0.194 (Lake Manitoba), and 2.701 (Clay Lake). Mean methylmercury concentrations in eggs (mg/kg), converted from reported dry weight concentrations assuming an 85 percent moisture content, were approximately 0.001 (Lake Manitoba), 0.002 (Lake Winnipeg), and 0.148 (Clay Lake). In addition to any maternally transferred methylmercury, eggs and subsequent larvae were then exposed to varying concentrations of waterborne methylmercury. The experimental results demonstrated a significant decline in hatching success and embryonic heart rate with increasing exposures of waterborne methylmercury, for all three lake stocks. However, after statistically adjusting for waterborne methylmercury effects, the maternally transferred methylmercury in eggs was not significantly correlated with either hatching success or embryonic heart rate. The authors noted that hatching success in eggs from Clay Lake females declined with increasing egg methylmercury concentrations, although the trend was not significant, and suggested that a larger sample size may reveal statistically significant declines. For the purposes of this evaluation, the data from this study indicate that fish tissue methylmercury concentrations in trophic level 4 fish (0.182, 0.194 mg/kg) similar to those expected with the TRC should not result in maternally deposited egg concentrations associated with reduced hatching success.

The effects of dietary methylmercury on multiple reproductive endpoints was also examined by Hammerschmidt *et al*. (2002). Using fathead minnows (*Pimephales promelas*), the researchers measured gonadal development of males and females, spawning success, days to spawning, reproductive effort of females, developmental success of embryos, hatching success of embryos, survival of larvae, and growth of larvae. No reductions in growth or survival were seen in adult fish from any of the treatment groups, regardless of the tissue concentrations. Developmental and hatching success of embryos were not measurably affected by mercury concentrations in either the diets or bodies of parental fish. Similarly, larval survival and growth were not correlated with dietary or tissue methylmercury concentrations. However, in one of the treatment groups, female fish fed the same diet during Phases 1 and 2 (continuous exposure) exhibited reduced gonadal development (based on GSI) with increasing body burden mercury concentrations. No threshold for this effect was presented, but the whole body tissue concentration from the low dose group was approximately 0.68 mg/kg in females (converted from reported dry weights assuming 80% moisture in whole body). The reduced GSI in these fish led to lower egg production (average daily number of eggs laid per gram of female carcass) with increasing mercury concentrations in the adult tissues. Fish fed the same diet during Phases 1 and 2 also exhibited reduced spawning success compared to fish fed the control diet. Male and female fish fed the low dose diet showed an average tissue concentration of 0.625 mg/kg, and had a spawning success rate of only 46 percent. Fish fed the control diet had an average tissue concentration of 0.08 mg/kg, and had a spawning success rate of 75 percent. In fish fed the continuous exposure diets, the number of days to spawning increased with increasing tissue mercury concentrations. In females, days to spawning was also inversely related to gonadal development.

The tissue concentrations in fish fed the low dose diet (average 0.625 mg/kg) during Phases 1 and 2 were substantially above the levels expected for trophic level 3 fish when applying the TRC under either trophic level approach. However, the 0.625 mg/kg average value is similar to the concentration expected in trophic level 4 fish (0.66 mg/kg) under the Average Concentration Trophic Level Approach. Based on the fathead minnow findings described above, Hammerschmidt *et al*. (2002) concluded that methylmercury decreased reproduction in adult fathead minnows at dietary concentrations realistically encountered by predatory fishes in mercury contaminated waters, with the implication that exposed fish populations could be adversely affected by this reproductive impairment.

None of the data examined for this evaluation provided definitive answers regarding the level of protection for fish afforded by the TRC. The trophic level methylmercury concentrations expected from applying the TRC under both trophic level approaches appear to be well below observed adverse effects concentrations described in the scientific literature. However, the trophic level concentrations expected under the Average Concentration Trophic Level Approach, which are higher than those under the Highest Trophic Level Approach, are much closer to these adverse effects concentrations. Although the best currently available data suggest that the TRC would be sufficiently protective of listed fish, regardless of the trophic level approach used, the increasing emphasis on examining more subtle methylmercury-induced effects may reveal even

lower tissue-based threshold effects concentrations.

X.B. Reptiles and Amphibians

Evaluating the TRC with respect to reptile and amphibian species was more problematic than the evaluation for fish, birds, and mammals. The TRC was developed as a methylmercury limit in the edible tissues of fish and shellfish. The protectiveness of the TRC could then be evaluated for fish, based on toxicity associated with various fish tissue concentrations, or for piscivorous and omnivorous birds and mammals, based on the ingestion of methylmercury contaminated organisms. An evaluation for reptiles and amphibians can be based on ingestion if the species of concern feeds primarily on aquatic organisms and if there are sufficient data to establish reference doses, food ingestion rates, and dietary composition. If these species of concern do not feed on aquatic organisms, a risk assessment based solely on toxicity endpoints associated with known tissue mercury concentrations may be performed. However, this type of assessment cannot be used to evaluate the TRC, as there is currently no reliable way to compare tissue mercury concentrations in reptiles and amphibians with the various trophic level fish tissue concentrations expected from the two approaches. Too little is presently known about mercury bioaccumulation in reptiles and amphibians to allow for any comparative risk prediction capability based on bioaccumulation in fish. The majority of the information presented below on the ecotoxicology of metals in reptiles and amphibians is from a comprehensive review by Linder and Grillitsch (2000).

No reptile mortality due to metal intoxication has ever been reported (Linder and Grillitsch, 2000); however, relevant ecotoxicological data on the effects of mercury on reptiles is severely lacking. Of the available studies, most have focused on tissue metal concentrations in free-ranging animals without reference to the ambient conditions giving rise to those concentrations. However, studies showing the highest tissue levels of mercury and other metals were associated with areas apparently having a high degree of environmental contamination. Linder and Grillitsch (2000) reported that only a few studies examined laboratory exposure to a defined dose, and none of these involved mercury. In a later review, Campbell and Campbell (2001) reviewed 20 studies examining inorganic contaminants and snakes, and found one (Hopkins *et al*., 1999) that examined effects concentrations. Unfortunately, neither the Hopkins *et al*.(1999) study nor the follow-up study examining the effects of chronic dietary exposure to trace inorganic elements (Hopkins *et al*., 2002) involved mercury. The remaining 19 studies reviewed by Campbell and Campbell (2001) only examined mercury concentrations in snake tissues, with no connection to exposure or effects. Linder and Grillitsch (2000) found that the available data indicate reptiles in general do not biomagnify metals to an extent that would correspond to their trophic level. In one study comparing whole body mercury concentrations in biota from several trophic levels, Winger *et al*. (1984) reported mercury levels corresponding to trophic level, being consistently highest in water snakes (*Natrix* spp.) and little green herons (*Butorides virescens*). However, mercury levels in the garter snake (*Thamnophis sirtalis*) were among the lowest of several vertebrate species examined, with the highest levels in piscivorous birds (Dustman *et al*, 1972). Linder and Grillitsch (2000) also reported that the available literature appears to support

the hypothesis that reptiles exhibit a generally low sensitivity to metals. However, these authors caution against drawing definitive conclusions regarding reptiles and metal contaminants, due to the almost complete absence of toxicological research under fairly defined experimental conditions, and the absence of any information on embryotoxic potential.

The dietary habits of both snakes considered in this evaluation [San Francisco garter snake (*Thamnophis sirtalis tetrataenia*) and giant garter snake (*Thamnophis gigas*)] indicate a strong dependence on aquatic ecosystems. The San Francisco garter snake is known to prey on red-legged frogs (*Rana aurora*), Pacific tree frogs (*Hyla regilla*), California newts (*Taricha torosa*), western toads (*Bufo boreas*), threespine stickleback (*Gasterosteus aculeatus*), and mosquitofish (*Gambusia affinis*) (U.S. Fish and Wildlife Service, 1985c). Known prey items of the giant garter snake include mosquitofish, common carp (*Cyprinus carpio*), Sacramento blackfish (*Orthodon microlepidouts*), and bullfrogs (*Rana catesbiana*) (U.S. Fish and Wildlife Service, 1999). It is reasonable to assume these snakes may also prey on other available fish and frog species.

These dietary habits clearly indicate that both snakes may be exposed to methylmercury through ingestion of fish and other aquatic-dependent prey. However, evaluating the effect of the TRC on these snakes based on ingestion of methylmercury contaminated prey is confounded by the lack of necessary data. Although it is possible to estimate a daily food ingestion rate for snakes from Nagy (2001) and to make assumptions regarding the trophic level composition of the diet, the existing toxicological data on snakes do not allow for determination of any reference dose. Without a scientifically determined effects concentration in snakes, no WVs can be generated. While the physiological similarities between birds and reptiles may suggest it is possible to take the avian test dose used in this effort, make certain assumptions regarding inter-taxonomic uncertainty, and then arrive at some reference dose and WVs for these snakes, any conclusions drawn from the subsequent evaluation of the TRC would be highly speculative. The combination of reptilian physiological and life history characteristics (*e.g.*, long life span, small home ranges, high trophic position, and ectothermic physiology) make such an extrapolation inappropriate (Hopkins *et al.*, 2002). Nagy (2001) points out that the metabolic rate of reptiles results in daily food requirements drastically lower than both birds and mammals. A 1-kg reptile consumes only 9 percent of the amount eaten by a 1-kg bird and approximately 12 percent of the amount a 1-kg mammal requires. If snakes are no more sensitive to ingested methylmercury than are birds (*i.e.*, having the same reference dose), then the lower daily food ingestion rate resulting from the snake's metabolic needs might suggest that fish tissue methylmercury levels that are protective of birds should also be protective of snakes. Although the limited ecotoxicological data presented above may suggest that reptiles in general are less sensitive to methylmercury than other taxa, no definitive conclusions can be made regarding the protectiveness of the TRC for these species until dietary methylmercury effects concentrations can be established for snakes.

The toxicity of mercury has been studied to a much greater extent with amphibians than with reptiles. Most amphibian species have aquatic-dependent early life stages where exposure may be dominated by direct uptake of dissolved metals from water, while exposure through dietary

sources may become more predominant in the subsequent adult life stages (Linder and Grillitsch, 2000). The majority of available effects data for amphibians come from acute and chronic toxicity studies with early life stages of frogs, using waterborne concentrations of inorganic mercury (Linder and Grillitsch, 2000; U.S. Environmental Protection Agency, 1996; Birge *et al*., 1979). Lethality is the toxicological endpoint most commonly assessed in these studies, with the majority of embryo or larval LC50s (lethal concentration for 50% of test population) in the range of 10 - 100 ug/L (Linder and Grillitsch, 2000). It should be noted that several LC50s below 10 ug/L and above 100 ug/L have also been observed (Linder and Grillitsch, 2000; U.S. Environmental Protection Agency, 1996). Concentrations as low as 0.1 ug/L have resulted in up to 6 percent mortality of leopard frog (*Rana pipiens*) embryos (U.S. Environmental Protection Agency, 1996). Embryonic malformation is another commonly measured endpoint in mercury toxicity studies. Waterborne mercury concentrations associated with amphibian embryo malformations ranged from 2 - 75 ug mercuric chloride/L, with malformation rates ranging from 5 to greater than 10 percent (Birge *et al*., 1983).

Adverse effects have also been reported for amphibians exposed to methylmercuric chloride (U.S. Environmental Protection Agency, 1996). Concentrations of methylmercuric chloride between 0 - 4 ug/L resulted in an EC50 (effects concentration for 50% of test population) for embryo deformities in leopard frogs. No metamorphosis was seen in leopard frog tadpoles exposed to concentrations between 1 - 10 ug/L for 3 to 4 months. Greater than 10 percent deformity and mortality was observed in larvae of the African clawed frog (*Xenopus laevis*) exposed to 0.3 ug/L for more than 10 days.

Based on the limited data available, it appears that the early life stages of amphibians are the most sensitive to metal exposures (Linder and Grillitsch, 2000). All of the waterborne effects concentrations for mercury reported above are considerably higher than environmentally realistic levels. Although there will likely be a great deal of variation between water bodies within California, the waterborne concentrations of mercury associated with the TRC should be orders of magnitude below any of the effects concentrations described here. However, these water concentration toxicity data are insufficient to fully characterize risk from the TRC as they do not take into account dietary exposure in post-embryolarval stages or the potential for maternal transfer of bioaccumulated methylmercury into the eggs. Preliminary results from designed studies suggest that metals bioaccumulated into female amphibians may be depurated during egg development and laying (Linder and Grillitsch, 2000). This process, in combination with exposure through waterborne concentrations, could be toxicologically relevant for the embryolarval stages of amphibians.

Due to methylmercury's propensity to bioaccumulate throughout the lifetime of an animal that is dependent on the aquatic food chain, adverse effects in adult life stages may be possible from relatively low prey concentrations. Unfortunately, the effects of dietary exposure to methylmercury in later life stages of amphibians have not been adequately explored. The literature on the bioaccumulation of metals in amphibians is less developed than for reptiles, with only a few controlled experiments examining bioaccumulation from dietary sources (Linder and

Grillitsch, 2000). No data were found in the scientific literature specifically regarding mercury bioaccumulation in frogs, the only amphibian taxon considered in this evaluation of the TRC. However, the limited data on the uptake of metals by amphibians suggest that the bioaccumulation of methylmercury may be an important exposure pathway for frogs.

The single amphibian considered in this evaluation, the California red-legged frog (*Rana aurora draytonii*), feeds as an adult on both invertebrates and vertebrates. Vertebrate prey, such as the Pacific tree frog (*Hyla regilla*) and California mouse (*Peromyscus californicus*), can account for over half of the dietary biomass in large adults (U.S. Fish and Wildlife Service, 2002). It is not known how much of the frog's diet may be comprised of aquatic invertebrates, or whether small fish are ever consumed. The consumption of Pacific tree frogs may constitute an important methylmercury exposure pathway, if they are closely linked with a contaminated aquatic environment.

As discussed previously, the impact of the TRC can only be reliably evaluated for non-fish organisms if they feed on aquatic prey (*i.e.*, fish or aquatic invertebrates) and if there are sufficient data to determine an appropriate dietary test dose at which adverse effects in the organisms are observed. Although California red-legged frogs may consume substantial numbers of aquatic prey, the literature on amphibian ecotoxicology revealed no information indicating that any research has been done involving the effects of dietary exposure to mercury in amphibians (Linder and Grillitsch, 2000; U.S. Environmental Protection Agency, 1996; Birge *et al*., 1979). This lack of data eliminates the possibility of evaluating the TRC for red-legged frogs using a methylmercury ingestion approach.

The methodology used in this evaluation of the TRC is based on the assumption that upper trophic level wildlife species (*i.e.*, piscivorous and omnivorous birds and mammals) have the greatest inherent risk from exposure to methylmercury. No currently available information was found to contradict this assumption, although an increasing emphasis on ecotoxicological research with reptiles and amphibians may provide new data with which to compare these inter-taxonomic sensitivities. Consumption of aquatic organisms by the California red-legged frog and the two species of garter snakes may expose them to toxicologically relevant concentrations of methylmercury, although possibly less so than in those species (*e.g.*, piscivorous birds and mammals) with a greater daily dietary reliance on aquatic prey. The available scientific literature strongly suggests that both reptiles and amphibians can bioaccumulate methylmercury, although the degree to which this occurs has not been fully characterized. However, until the appropriate toxicological data are generated, no definitive conclusions can be drawn about the protectiveness of either TRC trophic level approach for the California red-legged frog, San Francisco garter snake, or giant garter snake.

XI. DISCUSSION

As explained previously, the objective of this effort was to evaluate whether promulgation of the EPA's human health criterion for methylmercury may affect any federally listed threatened or endangered species in California. To do this, a risk assessment methodology was developed and used to analyze the potential effect of the TRC on several of these listed species. The species selected for analysis were presumed to be at the greatest risk of dietary exposure, due to their high trophic position and/or dietary dependence on the aquatic ecosystem. The results of these analyses indicate that some of these species should be sufficiently protected against adverse effects from methylmercury toxicity, depending on the trophic level approach evaluated. For other species, the evaluation results suggest that the TRC may not be adequate to protect against adverse effects.

Risk assessments such as the one used in this effort are designed to gauge the *potential* for adverse effects. The WVs calculated in this document are assumed to represent protective dietary concentrations of methylmercury, at which no adverse effects are expected. Then, if the predicted DC value for any given species is at or below the corresponding WV, it may be concluded with reasonable confidence that adverse effects to that species are not likely to occur. In contrast, a DC value higher than the corresponding WV only results in a presumption of risk for adverse effects. This is due to the fact that WVs are derived from toxicity data for surrogate species, with various assumptions about interspecific sensitivities, dietary composition of the species of concern, and the use of uncertainty factors to estimate a dose at which no adverse effects should occur. Therefore, any presumption of risk for a species can only be definitively confirmed or dismissed by available scientific evidence that serves to remove these layers of uncertainty.

The Service's Environmental Contaminants Division believes the analyses presented in this document represent the most current state of knowledge regarding the risk to California's listed species from dietary methylmercury. The mammalian and avian test doses used in this effort, which serve as the toxicological foundation for this methodology, remain the best available benchmarks of effects concentrations for these taxonomic groups. Uncertainty factors have previously been applied to these test doses, initially for the GLI and then updated for the MSRC (U.S. Environmental Protection Agency, 1995d; 1997a, respectively), to establish reference doses for key piscivorous wildlife species at which no adverse effects would be expected. To date, no new evidence has been presented suggesting that the uncertainty factors used for this evaluation should be altered to establish higher reference doses for any of the species considered. In several cases, the dietary compositions used in species evaluations were based on limited empirical data; however, until new data are generated, these compositions remain the most reliable estimates. Finally, future controlled methylmercury dosing experiments with individuals of the species evaluated could potentially yield more accurate reference doses (*i.e.*, NOAELs); however, any such experiments are highly unlikely due to the regulatory status of these species as threatened or endangered.

For the reasons cited above, we believe the presumption of risk for certain species indicated by the results of our evaluation cannot presently be dismissed by the available scientific evidence. Those species for which the predicted DCs are significantly above the corresponding WVs (*i.e.*, >10% higher) would be considered at risk for adverse effects from methylmercury toxicity. Conclusions about the protectiveness of the TRC for each species, under both trophic level approaches evaluated, are summarized below in Table 8. These conclusions reflect the interpretation of the evaluation results by the Service's Environmental Contaminants Division only, and are not intended to represent the views of those EPA or Service scientists who helped develop the risk assessment methodology. In addition, these conclusions do not constitute the results of consultation under Section 7 of the ESA.

Table 8. Protectiveness of Tissue Residue Criterion for Seven California Species

Is the TRC Protective for...	Southern Sea Otter	Ca. Least Tern	Ca. Clapper Rail	Light-footed Clapper Rail	Yuma Clapper Rail	Western Snowy Plover	Bald Eagle
Under Average Concentration TL Approach?	Yes	**No**	Yes	**No**	**No**	Yes	**No**
- with Alternate WV Generated from UF_A of 3?	na	na	**No**	**No**	**No**	Yes	na
Under Highest TL Approach?	Yes	**No**	Yes	Yes	**No**	Yes	Yes
- with Alternate WV Generated from UF_A of 3?	na	na	Yes	**No**	**No**	Yes	na

Applying the TRC under the Average Concentration Trophic Level Approach would place five of the seven listed species at risk for adverse effects: California least tern; California, light-footed, and Yuma clapper rails; bald eagle. Only the southern sea otter and western snowy plover would be sufficiently protected under this approach. Applying the TRC under the Highest Trophic Level Approach would place two of the seven species, California least tern and Yuma clapper rail, at risk for adverse effects. The southern sea otter, California clapper rail, western snowy plover, and bald eagle should be sufficiently protected under this approach. No conclusions can be drawn at this time regarding the light-footed clapper rail, due to remaining uncertainty about this subspecies' sensitivity to methylmercury.

The two species determined to still be at risk under the Highest Trophic Level Approach are the California least tern and the Yuma clapper rail. As explained previously in this document, the methodology outlined in the Average Concentration Trophic Level Approach can be used to calculate the trophic level-specific methylmercury concentrations necessary to maintain any species' DC at or below its calculated WV. Using Equation 3 from this methodology and substituting any WV for the DC term, we can solve for the methylmercury concentration in trophic level 2 prey:

FDTL2 = WV / [(%TL2) + (%TL3 × MTL3) + (%TL4 × MTL3 × MTL4)]

Once the trophic level 2 concentration is calculated, the remaining trophic levels can be determined using our established food chain multiplier relationships:

FDTL3 = FDTL2 × MTL3
FDTL4 = FDTL3 × MTL4

Using the WVs determined for the least tern and Yuma clapper rail, along with the trophic level composition of their diets, the trophic level methylmercury concentrations required to maintain these WVs can be calculated (Table 9).

Table 9. Trophic Level Methylmercury Concentrations Calculated for California Least Tern and Yuma Clapper Rail

	California Least Tern (WV = 0.030 mg/kg)	Yuma Clapper Rail (WV generated with UF_A of 1 = 0.040 mg/kg)	Yuma Clapper Rail (WV generated with UF_A of 3 = 0.013 mg/kg)
FDTL2	0.005 mg/kg	0.009 mg/kg	0.003 mg/kg
FDTL3	0.030 mg/kg	0.053 mg/kg	0.017 mg/kg
FDTL4	0.120 mg/kg	0.210 mg/kg	0.068 mg/kg

Of the two approaches evaluated, the Highest Trophic Level Approach affords a greater degree of protection for California's listed bird and mammal species than the Average Concentration Trophic Level Approach. As stated previously, the best currently available data on mercury toxicity in fish suggest that the TRC under either approach should be sufficiently protective of all listed fish in California; however, the trophic level concentrations expected under the Average Concentration Trophic Level Approach would be much closer to observed adverse effects concentrations described in the scientific literature. Finally, although a lack of relevant data precludes any conclusions regarding the potential impact of the TRC on the reptile and amphibian species considered, the lower trophic level concentrations expected under the Highest Trophic Level Approach would afford a greater measure of protection than those expected under

the Average Concentration Trophic Level Approach. Based on the above conclusions, we believe that the TRC would not adequately protect all listed species in California; however, applying the TRC under the Highest Trophic Level Approach would reduce the number of species at risk.

Finally, it must be noted that the risk assessment methodology presented in this document was not applied to any wildlife species other than the federally listed species from the Appendix. However, other non-listed wildlife may be potentially at risk under the TRC, due to their dietary dependence on aquatic ecosystems. Using the same approach followed in this effort, regulatory agencies should be able to determine whether concentrations of methylmercury in fish tissue under the TRC may also pose a risk to these non-listed wildlife species.

XII. REFERENCES

XII.A. LITERATURE CITED

Abt Associates, Inc. 1995. Review and analysis of toxicity data to support the development of uncertainty factors for use in estimating risks of contaminant stressors to wildlife. Bethesda, Maryland. Prepared for the U.S. Environmental Protection Agency, Office of Water. Washington, DC EPA Contract No. 68-C3-0332.

Albertson, J.D. 1995. Ecology of the California clapper rail in South San Francisco Bay. M.A. Thesis, San Francisco State University.

Allen, A. 1934. The season: San Francisco region. Bird-Lore. 36:316.

American Ornithologists' Union. 1957. Check-List of North American Birds, 5th ed. American Ornithologists' Union, Washington, D.C.

Anderson, B.W. and R.D. Ohmart. 1985. Habitat use by Clapper Rails in the Lower Colorado River Valley. Condor. 87:116-126.

Anthony, R.G., and F.B. Isaacs. 1981. Characteristics of bald eagle nest sites in Oregon. J. Wildl. Manage. 53(1):148-159.

Atwater, B., S. Conrad, J. Dowden, C. Hedel, R. MacDonald, and W. Savage. 1979. History, landforms, and vegetation of the estuary's tidal marshes. *In* T.J. Conomos (ed.): San Francisco Bay, the urbanized estuary. Pacific Div., Am. Assoc. for the Adv. of Sci. 58th annual mtg., S.F. State Univ., June 12-16, 1977.

Atwood, J.L. and D.E. Minsky. 1983. Least tern foraging ecology at three major California breeding colonies. Western Birds. 14:57-72.

Atwood, J.L. and P.R. Kelly. 1984. Fish dropped on breeding colonies as indicators of least tern food habits. Wilson Bulletin. 96(1):34-47.

Austin, J.E. and M.R. Miller. 1995. Northern Pintail (*Anas acuta*). *In* The Birds of North America, No. 163 (A. Poole and F. Gill, eds.) The Academy of Natural Sciences, Philadelphia, and The American Ornithologists' Union, Washington, D.C. 32 pp.

Barnes, R.D. 1980. Invertebrate Zoology 4th Ed. Saunders College Publishing, Philadelphia, PA. 1050 pp.

Barr, J.F. 1986. Population dynamics of the common loon (*Gavia immer*) associated with mercury-contaminated waters in northwestern Ontario. Canadian Wildlife Service. Occasional Paper, No. 56, 23 pp.

Bennett, W.W. and R.D. Ohmart. 1978. Habitat Requirements and Population Characteristics of the Clapper Rail (*Rallus longirostris yumanensis*) in the Imperial Valley of California. A report submitted to the Univ. of California Lawrence Livermore Laboratory.

Bent, A.C. 1921. Life histories of North American gulls and terns. U.S. Natl. Mus. Bull. 113.

Birge, W.J., J.A. Black, A.G. Westerman, and J.E. Hudson. 1979. The effects of mercury on reproduction of fish and amphibians, Chapter 23 *in* J.O. Nriagu (ed.) The Biogeochemistry of Mercury in the Environment. Elsevier Press, New York. pp. 629-655.

Birge, W.J., J.A. Black, A.G. Westerman, and B.A. Ramey. 1983. Fish and amphibian embryos: a model system for evaluating teratogenicity. Fundamentals of Applied Toxicology. 3:237-242.

Boening, D.W. 2000. Ecological effects, transport, and fate of mercury: a general review. Chemosphere. 40:1335-1351.

Bouton, S.N., P.C. Frederick, M.G. Spalding, and H. McGill. 1999. Effects of chronic, low concentrations of dietary methylmercury on the behavior of juvenile great egrets. Environmental Toxicology and Chemistry. 18(9):1934-1939.

Breteler, R.J., I. Valiela, and J.M. Teal. 1981. Bioavailability of mercury in several north-eastern U.S. *Spartina* ecosystems. Estuarine, Coastal, and Shelf Science. 12:155-166.

Brisbin, I.L., Jr. and T.B. Mowbray. 2002. American Coot (*Fulica americana*) and Hawaiian Coot (*Fulica alai*). *In* The Birds of North America, No. 697 (A. Poole and F. Gill, eds.). The Birds of North America, Inc., Philadelphia, PA 44 pp.

Buehler, D.A. 2000. Bald Eagle (*Haliaeetus leucocephalus*). *In* The Birds of North America, No. 506 (A. Poole and F. Gill, eds.). The Birds of North America, Inc., Philadelphia, PA. 40 pp.

Buchanan, G.A., D.W. Russell,, and D.A. Thomas. 2001. Derivation of New Jersey-specific wildlife values as surface water quality criteria for: PCBs, DDT, Mercury. Multi-agency report by: U.S. Fish and Wildlife Service, Pleasantville, NJ; U.S. Environmental Protection Agency, Edison, NJ; New Jersey Department of Environmental Protection, Trenton, NJ. 36 pp.

Burger, J. and M. Gochfeld. 1997. Risk, mercury levels, and birds: Relating adverse laboratory effects to field biomonitoring. Environmental Research. 75:160-172.

California Department of Fish and Game. 1976. A proposal for sea otter protection and research and request for the return of management to the State of California (DRAFT). 255 pp.+ appendices.

_____. 1990. 1989 Annual Report on the Status of California's Listed Threatened and Endangered Plants and Animals. Sacramento, California.

_____. 1991. 1990 Annual Report on the Status of California's Listed Threatened and Endangered Plants and Animals. Sacramento, California. 203pp.

_____. 2001. Bald eagles in California. California Department of Fish and Game, Habitat Conservation Planning Branch, California's Plants and Animals. Internet address: www:dfg.ca.gov/hcpb/species/.

_____. 2001. California's living marine resources: a status report. University of California Publication No. SG01-11. Internet address: www.dfg.ca.gov/mrd.

California Regional Water Quality Control Board, Central Valley Region. 2002. Clear Lake TMDL for Mercury, Final Staff Report. California Environmental Protection Agency, Regional Water Quality Control Board, Central Valley Region, Sacramento, California. 62 pp+ appendices.

Campbell, K.R. and T.S. Campbell. 2001. The accumulation and effects of environmental contaminants on snakes: a review. Environmental Monitoring and Assessment. 70:253-301.

Canadian Council of Ministers of the Environment. 2000. Canadian tissue residue guidelines for the protection of wildlife consumers of aquatic biota: Methylmercury. *In* Canadian environmental quality guidelines, 1999, Canadian Council of Ministers of the Environment, Winnipeg.

Chandik, T. and A. Baldridge. 1967. Nesting season, middle Pacific Coast region. Audubon Field Notes. 21:600-603.

Charbonneau, S.M., I.C. Munro, E.A. Nera, R.F. Willes, T. Kuiper-Goodman, F. Iverson, C.A. Moodie, D.R. Stoltz, F.A.J. Armstrong, J.F. Uthe, and H.C. Grice. 1974. Subacute toxicities of methylmercury in the adult cat. Toxic. Appl. Pharm. 27:569-581.

Chase, T. and R.O. Paxton. 1965. Middle Pacific Coast region. Audubon Field Notes. 19:574-576.

Conway, C.J., W.R. Eddleman, S.H. Anderson and L.R. Hanebury. 1993. Seasonal changes in Yuma clapper rail vocalization rate and habitat use. J. Wild. Manage. 57(2):282-290.

Cullen, S.A., J.R. Jehl Jr., and G.L. Nuechterlein. 1999. Eared Grebe (*Podiceps nigricollis*). *In* The Birds of North America, No. 433 (A. Poole and F. Gill, eds.). The Birds of North America, Inc., Philadelphia, PA 28 pp.

Dansereau, M., N. Lariviere, D. Du Tremblay, D. Belanger. 1999. Reproductive performance of two generations of female semidomesticated mink fed diets containing organic mercury contaminated freshwater fish. Arch. Environ. Contam. Toxicol. 36:221-226.

Dawson, W.L. 1924. The birds of California. South Moulton Company, San Diego, California.

Dedrick, K. 1993. San Francisco Bay tidal marshland acreages: recent and historic values. In O.T. Magoon (ed.): Proceedings of the Sixth Symposium on Coastal and Ocean Management (Coastal Zone '89). Charleston, South Carolina, July 11-14, 1989. Publ. by Am. Society of Civil Eng.

DeGraaf, R.M., V.E. Scott, R.H. Hamre, L. Ernst, and S.H. Anderson. 1991. Forest and Rangeland Birds of the United States. Natural History and Habitat Use. USDA Forest Service, Agriculture Handbook 688. 625 pp.

DeGroot, D.S. 1927. The California clapper rail: its nesting habits, enemies and habitat. Condor. 29(6): 259-270.

Detrich, P.J. 1981. Historic range of breeding bald eagles in California. Unpublished Manuscript. Redding, CA. 17 pp.

_____. 1982. Results of California winter bald eagle survey - 1982. U.S. Fish and Wildlife Service, Sacramento, CA. 16 pp.

Dunning, J. B. 1993. CRC handbook of avian body masses. CRC Press, Boca Raton, FL. 371 pp.

Dustman, E.H., L.F. Stickel, and J.B. Elder. 1972. Mercury in wild animals at Lake St. Clair, 1970, *in* R. Hartung and R.D. Dinman (eds.), Environmental Mercury Contamination. Ann Arbor, Michigan: Ann Arbor Science Publication. pp. 46-52.

Eadie, J.M., M.L. Mallory, and H.G. Limsden. 1995. Common Goldeneye (*Bucephala clangula*). *In* The Birds of North America, No. 170 (A. Poole and F. Gill, eds.). The Academy of Natural Sciences, Philadelphia, and The American Ornithologists' Union, Washington, D.C. 32 pp.

Eagles-Smith, C.A., T.H. Suchanek, P.B. Moyle, and D.W. Anderson. (in prep). Bacteria to birds: mercury trophic transfer efficiency as a function of trophic complexity. In prep. for submittal to Ecosystems.

Eddleman, W.R. 1989. Biology of the Yuma Clapper Rail in the Southwestern U.S. and Northwestern Mexico. U.S. Bureau of Reclamation, IA No. 4 -AA-30-020060.

Eddleman, W.R., and C.J. Conway. 1994. Clapper Rail, Chapter 12 *in* T.C. Tacha and C.E. Braun (eds.): Migratory Shore and Upland Game Bird Management in North America. International Association of Fish and Wildlife Agencies, in cooperation with the U.S. Dept. of the Interior, Fish and Wildlife Service; ASIN: 0935868755. Allen Press, Lawrence, Kansas. 223 pp.

Eisler, R. 2000. Mercury, Chapter 5 *in* Handbook of Chemical Risk Assessment: Health Hazards to Humans, Plants, and Animals, Vol. 1: Metals. Lewis Publishers, CRC Press, Boca Raton, FL. pp. 313-391.

Elbert, R.A. 1996. Reproductive performance and mercury exposure of birds at Clear Lake, CA. MS Thesis. University of California-Davis, Davis, California, USA. 70 pp.+ appendices.

Elbert, R.A. and D.W. Anderson. 1998. Mercury levels, reproduction, and hematology in Western grebes from three California lakes, USA. Environmental Toxicology and Chemistry. 17(2):210-213.

Elliot, M.L. and W.J. Sydeman. 2002. Breeding status of the California least tern at Alameda Point (former Naval Air Station, Alameda), Alameda, California, 2001. Unpublished Report, Point Reyes Bird Observatory, Stinson Beach, California. 57 pp.

Ellis, R.W. and L. Eslick. 1997. Variation and range of mercury uptake into plants at a mercury-contaminated abandoned mine site. Bull. Environ. Contam. Toxicol. 59:763-769.

Estes, J.A. 1990. Growth and equilibrium in sea otter populations. Journal of Animal Ecology. 59:385-401.

Evens, J., and G. Page. 1983. The ecology of rail populations at Corte Madera Ecological Reserve: with recommendations for management. A report to Marin Audubon Society from Point Reyes Bird Observatory. 62 pp.

Evers, D.C., O.P. Lane, C. DeSorbo, and L. Savoy. 2002. Assessing the impacts of methylmercury on piscivorous wildlife using a wildlife criterion value based on the Common loon, 1998-2001. Report BRI 2002-08, submitted to the Maine Department of Environmental Protection. Biodiversity Research Institute, Falmouth, Maine.

Fimreite, N. 1971. Effects of dietary methylmercury on ring-necked pheasants. Can. Wildl. Serv. Occas. Pap. 9. 39pp.

Fimreite N., 1974. Mercury contamination of aquatic birds in northwestern Ontario. J. Wild. Manage. 38(1):120-131.

Fjeld, E., T.O. Haugen, and L.A. Vollestad. 1998. Permanent impairment in the feeding behavior of grayling (*Thymallus thymallus*) exposed to methylmercury during embryogenesis. The Science of the Total Environment. 213:247-254.

Foerster, K.S., and J.E. Takekawa. 1991. San Francisco Bay National Wildlife Refuge Predator Management Plan and Final Environmental Assessment. Unpublished report.

Foerster, K.S., J.E. Takekawa, and J.D. Albertson. 1990. Breeding density, nesting habitat, and predators of the California clapper rail. Final report SFBNWR-11640-90-1, prepared for San Francisco Bay National Wildlife Refuge. Newark, CA.

Frenzel, R.W. 1984. Environmental contaminants and ecology of bald eagles in southcentral Oregon. PhD Thesis, Oregon State University. 119 pp.

Friedmann, A.S., M.C. Watzin, J.C. Leiter, and T. Brinck-Johnsen. 1996a. Effects of environmental mercury on gonadal function in Lake Champlain northern pike (*Esox lucius*). Bull. Environ. Contam. Toxicol. 56:486-492.

Friedmann, A.S., M.C. Watzin, T. Brinck-Johnsen, and J.C. Leiter. 1996b. Low levels of dietary methylmercury inhibit growth and gonadal development in juvenile walleye (*Stizostedion vitreum*). Aquatic Toxicology. 35:265-278.

Friedmann, A.S., E.K. Costain, D.L. MacLatchy, W. Stansley, and E.J. Washuta. 2002. Effect of mercury on general and reproductive health of largemouth bass (*Micropterus salmoides*) from three lakes in New Jersey. Ecotoxicology and Environmental Safety. 52:117-122.

Gill, F.B. 1995. Ornithology. W.H. Freeman and Company. 615 pp+ appendix.

Grinnell, J. 1928. A distributional summation of the ornithology of lower California. Univ. Calif. Publ. Zool. 32:1-300.

Grinnell, J., H.C. Bryant, and T.I. Storer. 1918. The game birds of California. University of California Press, Berkeley.

Grinnell, J. and M.W. Wythe. 1927. Directory of the bird-life of the San Francisco Bay region. Pacific Coast Avifauna. 18:1-160.

Grinnell, J. and A. Miller. 1944. The Distribution of the Birds of California. Pacific Coast Avifauna Number 27. Cooper Ornithological Club, Berkeley, California. Reprinted by Artemisia Press, Lee Vining, California; April 1986. 617 pp.

Gupta, M. and P. Chandra. 1998. Bioaccumulation and toxicity of mercury in rooted-submerged macrophyte *Vallisneria spiralis*. Environmental Pollution. 103:327-332.

Hammerschmidt, C.R., J.G. Wiener, B.E. Frazier, and R.G. Rada. 1999. Methylmercury content of eggs in yellow perch related to maternal exposure in four Wisconsin lakes. Environ. Sci. Technol. 33:999-1003.

Hammerschmidt, C.R., M.B. Sandheinrich, J.G. Wiener, and R.G. Rada. 2002. Effects of dietary methylmercury on reproduction of fathead minnows. Environ. Sci. Technol. 2002. 36:877-883.

Harvey, T.E. 1988. Breeding biology of the California clapper rail in south San Francisco Bay. 1988 Transactions of the Western Section of the Wildlife Society. 24:98-104.

Haywood, D.D. and R.D. Ohmart. 1986. Utilization of benthic-feeding fish by inland breeding bald eagles. Condor. 88:35-42.

Heinz G.H., 1979. Methylmercury: reproductive and behavioral effects on three generations of mallard ducks. J. Wildl. Manage. 43(2):394-401.

Henny, C.J., E.F. Hill, D.J. Hoffman, M.G. Spalding, and R.A. Grove. 2002. Nineteenth century mercury: hazard to wading birds and cormorants of the Carson River, Nevada. Ecotoxicology. 11:213-231.

Hopkins, W.A., C.L. Rowe, and J.D. Congdon. 1999. Elevated trace element concentrations and standard metabolic rate in banded water snakes, *Nerodia fasciata*, exposed to coal combustion wastes. Environmental Toxicology and Chemistry. 18:1258-1263.

Hopkins, W.A., J.H. Roe, J.W. Snodgrass, B.P. Staub, B.P. Jackson, and J.D. Congdon. 2002. Effects of chronic dietary exposure to trace elements on banded water snakes (*Nerodia fasciata*). Environmental Toxicology and Chemistry. 21(5):906-913.

Hothem, R.L. and A.N. Powell. 2000. Contaminants in eggs of Western snowy plovers and California least terns: is there a link to population declines? Bull. Environ. Contam. Toxicol. 65:42-50.

Hunt, W.G., J.M. Jenkins, R.E. Jackman, C.G. Thelander, and A.T. Gerstell. 1992. Foraging ecology of bald eagles on a regulated river. J. Raptor Res. 26(4):243-256.

Jackman, R.E., W.G. Hunt, J.M. Jenkins, and P.J. Detrich. 1999. Prey of nesting bald eagles in northern California. Journal of Raptor Research 33(2): 87-96.

Jarvinen, A.W. and G.T. Ankley. 1999. Linkage of effects to tissue residues: development of a comprehensive database for aquatic organisms exposed to inorganic and organic chemicals. Pensacola, Florida: Society of Environmental Toxicology and Chemistry (SETAC). 364 pp.

Jurek, R.M. 1988. Five-year status report. Bald Eagle. Calif. Dept. Fish and Game. Sacramento, CA. 15 pp.

_____. 2000. Unpublished data presented by Jan Johnson, U.S. Fish and Wildlife Service, Falconifornes of Northern California: Natural History and Management Workshop. October 24-26, 2000, North Coast Inn, Arcata, CA. The Wildlife Society, California North Coast Chapter, Arcata CA.

Knight, R.L., P.J. Randolph, G.T. Allen, L.S. Young, and R.J. Wigen. 1990. Diets of nesting bald eagles, *Haliaeetus leucocephalus*, in western Washington. Canadian Field-Naturalist. 104(4):545-551.

Kozie, K.D. and R.K. Anderson. 1991. Productivity, diet, and environmental contaminants in bald eagles nesting near the Wisconsin shoreline of Lake Superior. Arch. Environ. Contam. Toxicol. 20:41-48.

Kozloff, E.N. 1990. *Invertebrates*. Saunders College Publishing, Philadelphia, PA. 843 pp.

Kvitek, R.G. and J.S. Oliver. 1988. Sea otter foraging and effects on prey populations and communities in soft-bottom environments, Chapter 3 *in* G.R. VanBlaricom and J.A. Estes (eds.), The Community Ecology of Sea Otters. Springer-Verlag, Berlin, Germany. pp. 22-45.

Latif, M.A., R.A. Bodaly, T.A. Johnston, and R.J.P. Fudge. 2001. Effects of environmental and maternally derived methylmercury on the embryonic and larval stages of walleye (*Stizostedion vitreum*). Environmental Pollution. 111:139-148.

Lehman, R.N. 1979. A survey of selected habitat features of 95 bald eagle nest sites in California. Calif. Dept. Fish and Game. Wildlife Management Branch Administrative Report No. 79-1. Sacramento, CA. 21 pp.

Lehman, D.E. Craigie, P.L. Colins, and R.S. Griffen. 1980. An analysis of habitat requirements and site selection criteria for nesting bald eagles in California. Report by Wilderness Research Institute, Arcata, CA., for U.S. Forest Service, Region 5. San Francisco, CA. 106 pp.

Linder, G. and Grillitsch. 2000. Ecotoxicology of metals, Chapter 7 *in* D.W. Sparling, G. Linder, and C.A. Bishop (eds.), Ecotoxicology of Amphibians and Reptiles. Pensacola, Florida: Society of Environmental Toxicology and Chemistry (SETAC). 904 pp.

Massey, B.W. 1974. Breeding biology of the California least tern. Proc. Linnaean Soc. 72:1-24.

Massey, B., R. Zembal, and P. Jorgensen. 1984. Nesting habitat of the light-footed clapper rail in southern California. Journal of Field Ornithology 55: 67-80.

Matta, M.B., J. Linse, C. Cairncross, L. Francendese, and R.M. Kocan. 2001. Reproductive and transgenerational effects of methylmercury or Aroclor 1268 on *Fundulus heteroclitus.* Environmental Toxicology and Chemistry. 20(2):327-335.

McKernan, R.L. and G. Braden. 1999. Status, distribution, and habitat affinities of the southwestern willow flycatcher along the LCR Year 3-1998. Submitted to U.S. Bureau of Reclamation, LCR region, Boulder City, Nevada and U.S. Fish and Wildlife Service, Carlsbad, CA.

Mersmann, T.J., D.A. Buehler, J.D. Fraser, and J.K.D. Seegar. 1992. Assessing bias in studies of bald eagle food habits. J. Wildl. Manage. 56(1):73-78.

Moffitt, J. 1941. Notes on the food of the California clapper rail. Condor 43:270-273.

Monson, G. And A. Phillips. 1981. Annotated checklist of the birds of Arizona. The University of Arizona Press, Tucson. 240 pp.

Morris, R.H., D.P. Abbott, and E.C. Haderlie (eds.). 1980. Intertidal Invertebrates of California. Stanford University Press, Stanford, CA. 658 pp.

Mowbray, T. 1999. American Wigeon (*Anas americana*). *In* The Birds of North America, No. 401 (A. Poole and F. Gill, eds.). The Birds of North America Inc., Philadelphia, PA 32 pp.

Moyle, P.B. 2002. Inland Fishes of California. University of California Press, Berkeley and Los Angeles, CA. 446 pp.

Nagy, K.A. 1987. Field metabolic rate and food requirement scaling in mammals and birds. Ecol. Monogr. 57:111-128.

Nagy, K.A. 2001. Food requirements of wild animals: predictive equations for free-living mammals, reptiles, and birds. Nutrition Abstracts and Reviews, Series B: Livestock Feeds and Feeding. 71(10):21R-31R.

NatureServe. 2001. Internet address: http://www/natureserve.org

Nevada Division of Wildlife. 1998. Comments on LCR MSCP Preliminary Species Conservation Goals: Bird Species. Prepared by C. Tomlinson, nongame biologist, Nevada Division of Wildlife, Las Vegas, Nevada.

Nichols, J, S. Bradbury, and J. Swartout. 1999. Derivation of wildlife values for mercury. Journal of Toxicology and Environmental Health, Part B, 2:325-355.

Norheim, G. and A. Froslie. 1978. The degree of methylation and organ distribution of mercury in some birds of prey in Norway. Acta Pharmacol. and Toxicol. 43:196-204.

Ohmart, R.D. and R.W. Smith. 1973. North American Clapper Rail (Rallus longirostris). Literature Survey With Special Consideration Being Given to the Past and the Present Status of *yumanensis*. USBR, Contract No. 14-06-300-2409.

Ohmart, R.D. and R.E. Tomlinson. 1977. Foods of western Clapper Rails. Wilson Bulletin. 89(2):332-336.

Page, G.W., L.E. Stenzel, W.D. Shuford, and C.R. Bruce. 1991. Distribution and abundance of the snowy plover on its western North American breeding grounds. J. Field Ornithol. 62(2):245-255.

Page, G.W., J.S. Warriner, J.C. Warriner, and P.W.C. Paton. 1995. Snowy Plover (*Charadrius alexandrinus*). *In* The Birds of North America, No. 154 (A. Poole and F.Gill, eds.). The Academy of Natural Sciences, Philadelphia, PA, and The Ornithologists' Union, Washington, D.C.

Palmer, R.S. (ed.). 1988. Handbook of North American Birds. Vols. 4 & 5. Yale University Press, New Haven, CT.

Patten, M.A., G. McCaskie, P. Unitt. In Press. Birds of the Salton Sea: Status, Biogeography, and Ecology.

Piest, L. And J. Campoy. 1998. Report of Yuma Clapper Rail Surveys at Cienega de Santa Clara, Sonora. Unpublished Report.

Pray, R.H. 1954. Middle Pacific Coast region. Audubon Field Notes. 8:326-327.

Proctor, N.S. and P.J. Lynch. 1993. Manual of ornithology: avian structure and function. Yale University Press. 340 pp.

Reidman, M.L. and J.A. Estes. 1988. A review of the history, distribution and foraging ecology of sea otters, Chapter 2. *in* G.R. VanBlaricom and J.A. Estes (eds.), The Community Ecology of Sea Otters. Springer-Verlag, Berlin, Germany. pp. 4-21.

Reidman, M.L. and J.A. Estes. 1990. The sea otter (*Enhydra lutris*): behavior, ecology, and natural history. Biological Report 90(14). U.S. Department of the Interior, Fish and Wildlife Service, Washington, D.C. 102 pp.

Rosenberg, K.V., R.D. Ohmart, W.C. Hunter, and B.W. Anderson. 1991. Birds of the LCR Valley. University of Arizona Press, Tucson, AZ.

Roth, V. and W. Brown. 1980. Arthropoda: Arachnida (Mites, Spiders, and Scorpions), Chapter 23 *in* R.C. Brusca (ed.), Common Intertidal Invertebrates of the Gulf of California. The University of Arizona Press, Tuscon, Arizona. pp. 347-355.

Ruhlen, T. and S. Abbott. 2000. Distribution, protection, and reproductive success of Snowy plovers at Point Reyes National Seashore in 2000. Point Reyes Bird Observatory, Stinson Beach, California.

Schwarzbach, S., . Henderson, and J.S. Albertson. 1996. Assessing risk from methyl mercury in tidal marsh sediments to reproduction of California clapper rails (*Rallus longirostris obsoletus*) using threshold diet and egg/sediment ratio approaches. Poster for Society of Environmental Toxicology and Chemistry, November 1996, Washington, D.C.

Schwarzbach, S. and T. Adelsbach. 2002. Assessment of ecological and human health impacts of mercury in the Bay-Delta watershed. Subtask 3B: Field assessment of avian mercury exposure in the Bay-Delta ecosystem. Final Report to the CALFED Bay-Delta Mercury Project, 39 pp.

Schwarzbach, S.E., J.D. Albertson, and C.M. Thomas. (in press). Factors affecting reproductive success of the California clapper rail (*Rallus longirostris obsoletus*) in San Francisco Bay. 34 pp.

Setmire, J.G., J.C Wolfe, and R.K. Stroud. 1990. Reconnaissance investigation of water quality, bottom sediment, and biota associated with irrigation drainage in the Salton Sea area, California, 1986-1987. U.S. Geological Survey Water-Resources Investigative Report, 89-4102.

Shepardson, D.I. 1909. Notes on the least tern. Oologist. 26:152.

Sibley, C.G. 1952. The birds of the south San Francisco Bay region. Oakland Public Museum. 42 pp.

Slotton, D.G., T.H. Suchanek, and S.M. Ayers. 2000. Delta wetlands restoration and the mercury question: year 2 findings of the CALFED UC Davis Delta mercury study. Contributed paper for the IEP Newsletter, Interagency Ecological Program for the San Francisco Estuary. 13(4):34-44.

Snyder, N.F. and J.W. Wiley. 1976. Sexual size dimorphism in hawks and owls of North America. Orni. Monogr. 20.

Spalding, M.G., P.C. Frederick, H.C. McGill, S.N. Bouton, and L.R. McDowell. 2000a. Methylmercury accumulation in tissues and effects on growth and appetite in captive great egrets. Journal of Wildlife Diseases. 36(3):411-422.

Spalding, M.G., P.C. Frederick, H.C. McGill, S.N. Bouton, L.J. Richey, I.M. Schumacher, C.G.M. Blackmore, and J. Harrison. 2000b. Histologic, neurologic, and immunologic effects of methylmercury in captive great egrets. Journal of Wildlife Diseases. 36(3):423-435.

Stalmaster, M. V., R. L. Knight, B. L. Holder, and R. J. Anderson. 1985. Bald eagles. Pps. 269-290 in E. R. Brown, ed. Management of wildlife and fish habitats in forests of western Oregon and Washington: Part 1- Chapter narratives. USDA Forest Service, Pacific North West Station, Portland, Oregon.

Stalmaster, M. V. and J. L. Kaiser. 1998. Effects of recreational activity on wintering bald eagles. Wildlife Monographs 137:1-46.

Storey, A., W. Montevecchi, H. Andrews, and N. Sims. 1988. Constraints on nest site selection: A comparison of predator and flood avoidance in four species of marsh-nesting birds (Genera: *Catoptrophorus*, *Larus*, *Rallus*, and *Sterna*). Journal of Comparative Psychology 102: 14-20.

Sykes, G. 1937. The Colorado Delta. *American Geographic Society Special Publication*, 19.

Thelander, C., and M. Crabtree. 1994. Life on the edge: a guide to California's endangered natural resources. Biosystem Books, Santa Cruz, CA. 550pp.

Thompson, B.C., J.A. Jackson, J. Burger, L.A. Hill, E.M. Kirsch, and J.L. Atwood. 1997. Least Tern (*Sterna antillarum*). *In* The Birds of North America, No. 290 (A. Poole and F. Gill, eds.). The Academy of Naturla Sciences, Philadelphia, PA, and The American Ornithologists' Union, Washington, D.C. 32 pp.

Thompson, D.R. 1996. Mercury in birds and terrestrial mammals, Chapter 14 *in* W.N. Beyer, G.H. Heinz, and A.W. Redmon-Norwood (eds.), Environmental Contaminants in Wildlife: Interpreting Tissue Concentrations. CRC Press, Lewis Publishers, Clemson, SC.

Tucker, M.A. and A.N. Powell. 1999. Snowy plover diets in 1995 at a coastal southern California breeding site. Western Birds. 30:44-48.

U.S. Bureau of Land Management. 2001. Revised Biological Opinion on Transportation and Delivery of Central Arizona Project Water to the Gila River Basin in Arizona and New Mexico and its Potential to Introduce and Spread Nonnative Aquatic Species, (2-21-90-F-119a). April 17.

U.S. Department of Energy. 1993. Toxicological Benchmarks for Wildlife. ES/ER/TM-86. Environmental Restoration Division, ORNL Environmental Restoration Program, Oak Ridge, TN. 55 pp + appendices.

_____. 1994. Toxicological Benchmarks for Wildlife: 1994 Revision. ES/ER/TM-86/R1. Health Sciences Research Division and Environmental Sciences Division, Oak Ridge, TN. 84 pp + appendices.

_____. 1995. Toxicological Benchmarks for Wildlife: 1995 Revision. ES/ER/TM-86/R2. Risk Assessment Program, Lockheed Martin Energy Systems, Inc., Oak Ridge, TN. 28 pp + appendices.

_____. 1996. Toxicological Benchmarks for Wildlife: 1996 Revision. ES/ER/TM-86/R3. Risk Assessment Program, Health Sciences Research Division, Oak Ridge, TN. 29 pp + appendices.

U.S. Department of the Interior. 1998. Guidelines for Interpretation of the Biological Effects of Selected Constituents in Biota, Water, and Sediment. Report No. 3

U.S. Environmental Protection Agency. 1993. Wildlife Exposure Factors Handbook, Volume I. EPA/600/R-93/187a. Office of Research and Development. Washington, DC

_____. 1995a. Trophic Level and Exposure Analyses for Selected Piscivorous Birds and Mammals, Volume I: Analyses of Species in the Great Lakes Basin. Office of Water. Washington, DC

_____. 1995b. Trophic Level and Exposure Analyses for Selected Piscivorous Birds and Mammals, Volume III: Appendices. Office of Water. Washington, DC

_____. 1995c. Great Lakes Water Quality Initiative Technical Support Document for Wildlife Criteria. EPA-820-B-95-009. Office of Water. Washington, DC

_____. 1995d. Great Lakes Water Quality Initiative Criteria Documents for the Protection of Wildlife. EPA-820-B-95-008. Office of Water. Washington, DC

_____. 1996. Amphibian toxicity data for water quality criteria chemicals. EPA/600/R-96/124. National Health Environmental Effects Research Laboratory, Corvallis, Oregon.

_____. 1997a. Mercury Study Report to Congress Volume VI: An Ecological Assessment for Anthropogenic Mercury Emissions in the United States. EPA-452/R-97-008. Office of Research and Development. Washington, DC

_____. 1997b. Mercury Study Report to Congress Volume VII: Characterization of Human Health and Wildlife Risks from Mercury Exposure in the United States. EPA-452/R-97-009. Office of Research and Development. Washington, DC

U.S. Fish and Wildlife Service. 1976. The literature of the western clapper rails. Special Scientific Report - Wildlife No. 194. U.S. Department of the Interior, Fish and Wildlife Service, Washington, D.C. 21 pp.

_____. 1983. Yuma Clapper Rail Recovery Plan. U.S. Fish and Wildlife Service, Albuquerque, New Mexico. 51 pp.

_____. 1984. The salt marsh harvest mouse/California clapper rail recovery plan. U.S. Fish and Wildlife Service, Portland, Oregon. 122 pp.+ appendices.

_____. 1985a. Recovery plan for the California least tern (*Sterna antillarum browni*). U.S. Fish and Wildlife Service, Portland, Oregon. 112 pp.

_____. 1985b. Recovery plan for the Light-footed Clapper Rail. U.S. Fish and Wildlife Service, Portland, Oregon. 121 pp.

_____. 1985c. Recovery plan for the San Francisco garter snake (*Thamnophis sirtalis tetrataenia*). U.S. Fish and Wildlife Service, Portland, Oregon. 77 pp.

_____. 1986. Recovery plan for the Pacific bald eagle. U.S. Fish and Wildlife Service, Portland, Oregon. 163 pp.

_____. 1999. Draft recovery plan for the Giant garter snake (*Thamnophis gigas*). U.S. Fish and Wildlife Service, Portland, Oregon. ix+ 192 pp.

_____. 2001. Western snowy plover (*Charadrius alexandrinus nivosus*) Pacific coast population draft recovery plan. U.S. Fish and Wildlife Service, Portland, Oregon. xix+ 630 pp.

_____. 2002. Recovery plan for the California Red-legged frog (*Rana aurora draytonii*). U.S. Fish and Wildlife Service, Portland, Oregon. viii+ 173 pp.

_____. 2003. Final revised recovery plan for the souther sea otter (*Enhydra lutris nereis*). U.S. Fish and Wildlife Service, Portland, Oregon. xi+ 165 pp.

U.S. Fish and Wildlife Service and National Marine Fisheries Service. 2000. Biological opinion on the effects of the U.S. Environmental Protection Agency's final promulgation of the California Toxics Rule on listed species and critical habitats in California. U.S. Department of the Interior, Fish and Wildlife Service, Sacramento, California and U.S. Department of Commerce, National Marine Fisheries Service, Long Beach, California. 236 pp.+ appendices.

U.S. Forest Service. 2000. Draft Bald Eagle Mangement Plan, Lassen National Forest, Recovery Zone 26, Lake Almanor Area, Lake Almanor and the Upper Feather River. Chester, CA. 30 pp.

Varoujean, D.H. 1972. A study of the California clapper rail in Elkhorn Slough, 1972. Report to the California Dept. of Fish and Game. 9 pp.

Vermeer, K., F.A.J. Armstrong, and D.R.M. Hatch. 1973. Mercury in aquatic birds at Clay Lake, Western Ontario. J. Wildl. Manage. 37(1):58-61.

Walsh, P.M. 1990. The use of seabirds as monitors of heavy metals in the marine environment, Chapter 10 *in* R.W. Furness and P.S. Rainbow (eds.), Heavy Metals in the Marine Environment. CRC Press, Boca Raton, Florida.

Wang, J.C.S. 1986. Fishes of the Sacramento-San Joaquin estuary and adjacent waters, California: A guide to the early life histories. Interagency Ecological Study Program for the Sacramento-San Joaquin Estuary. Tech. Rept. 9. (FS/B10-4ATR 86-9). Internet address: http://elib.cs.berkeley.edu/kopec/tr9/.

Warriner, J.S., J.C. Warriner, G.W. Page, and L.E. Stenzel. 1986. Mating system and reproductive success of a small population of polygamous snowy plovers. Wilson Bull. 98(1):15-37.

Webber, H.M. and T.A. Haines. 2003. Mercury effects on predator avoidance behavior of a forage fish, golden shiner (*Notemigonus crysoleucas*). Environmental Toxicology and Chemistry. 22(7):1556-1561.

West, J.M. and J.B. Zedler. 2000. Marsh-creek connectivity: fish use of a tidal salt marsh in southern California. Estuaries. 23(5):699-710.

Wiener, J. G. and D. J. Spry, 1996. Toxicological significance of mercury in freshwater fish, Chapter 13 *in* W.N. Beyer, G.H. Heinz, and A.W. Redmon-Norwood (eds.), Environmental Contaminants in Wildlife: Interpreting Tissue Concentrations. Special Publication of the Society of Environmental Toxicology and Chemistry, Lewis Publishers, Boca Raton Florida, USA. 494 pp.

Wiener, J.G. D.P. Krabbenhoft, G.H. Heinz, and A.M. Scheuhammer. 2002. Ecotoxicology of mercury, Chapter 16 *in* D.J. Hoffman, B.A. Rattner, G.A. Burton, Jr., and J. Cairns, Jr, (eds.), Handbook of Ecotoxicology, 2nd edition. CRC Press, Boca Raton, Florida, USA, pp. 409-463.

Wilbur, S. 1974. The status of the light-footed clapper rail. American Birds 28: 868-870.

Wilson, D.E., M.A. Bogan, R.L. Brownell, Jr., A.M. Burdin, and M.K. Maminov. 1991. Geographic variation in sea otters, *Enhydra lutris*. Journal of Mammalogy. 72(1):22-36.

Winger, P.V., C. Siekman, T.W. May, and W.W. Johnson. 1984. Residues of organochlorine insecticides, polychlorinated biphenyls, and heavy metals in biota from the Apalachicola River, Florida, 1978. J. Assoc. Off. Anal. Chem. 67:325-333.

Wobeser, G., N.O. Nielsen, and B. Schiefer. 1976a. Mercury and mink I. The use of mercury contaminated fish as food for ranch mink. Can. J. Comp. Med. 40:30-33.

Wobeser, G., N.O. Nielsen, and B. Schiefer. 1976b. Mercury and mink II. Experimental methyl mercury intoxication. Can. J. Comp. Med. 40:34-45.

Wolfe, M.F., S. Schwarzbach, and R. A. Sulaiman. 1998. Effects of mercury on wildlife: a comprehensive review. Environmental Toxicology and Chemistry. 17(2):146-160.

Wolfe, M.F. and D. Norman. 1998. Effects of waterborne mercury on terrestrial wildlife at Clear Lake: evaluation and testing of a predictive model. Environmental Toxicology and Chemistry. 17(2):214-227.

Wren, C.D., H.R. MacCrimmon, and B.R. Loescher. 1983. Examination of bioaccumulation and biomagnification of metals in a Precambrian shield lake. Water, Air, and Soil Pollution. 19:277-291.

Wren, C.D., D.B. Hunter, J.F. Leatherland, and P.M. Stokes. 1987. The effects of polychlorinated biphenyls and methylmercury, singly and in combination on mink. II: Reproduction and kit development. Arch. Environ. Contam. Toxicol. 16:449-454.

Zeiner, D. , W. Laudenslayer, Jr., K. Mayer, M. White. Editors. 1990. California's Wildlife. Volume 2. Birds. State of California, Department of Fish and Game. Sacramento, California. 731 pp.

Zembal, R. and J.M. Fancher. 1988. Foraging behavior and foods of the light-footed clapper rail. Condor. 90:959-962.

Zembal, R. 1989. The light-footed clapper rail (*Rallus longirostris levipes*). U.S. Fish and Wildlife Service Publication. 2pp.

Zembal, R., B. Massey, and J. Fancher. 1989. Movements and activity patterns of the light-footed clapper rail. Journal of Wildlife Management 53: 39-42.

Zembal, R., S. Hoffman, and J. Bradley. 1998. Light-footed clapper rail management and population assessment, 1997. California Dept. of Fish and Game, Bird and Mammal Conservation Program Rep. 98-01. 23pp.

Zembal, R., and S. Hoffman. 2001. Light-footed clapper rail management, study, and translocation, 2001. Report to Naval Base Ventura County, U.S. Fish and Wildlife Service, and California Dept. of Fish and Game. Report prepared for California State University, Long Beach Foundation and Eldorado Audubon Society, Long Beach, California.

XII.B. PERSONAL COMMUNICATIONS

Heinz, G.H. 2002, 2003. Wildlife Biologist. U.S. Department of the Interior, U.S. Geological Survey, Patuxent Wildlife Research Center, Laurel, Maryland.

Schwarzbach, S.E. 2003. Fish and Wildlife Administrator. U.S. Department of the Interior, U.S. Geological Survey, Western Ecological Research Center Headquarters, Sacramento, California.

APPENDIX Federally Listed Threatened (T) and Endangered (E) Species in California Potentially At Risk From Methylmercury in Aquatic Ecosystems

Birds:
(T) Bald Eagle
(E) California Least Tern
(E) California Clapper Rail
(E) Yuma Clapper Rail
(E) Light-Footed Clapper Rail
(T) Western Snowy Plover

Amphibians and Reptiles:
(T) California Red-Legged Frogs
(T) Giant Garter Snake
(E) San Francisco Garter Snake

Fish:
(T) Coho Salmon (and Critical Habitat)
- (T) Central CA (and Critical Habitat)
- (T) So. OR/Northern CA (and Critical Habitat)

(T&E) Chinook Salmon (and Critical Habitat)
- (T) Central Valley Spring ESU (and Critical Habitat)
- (T) CA Coast ESU (and Critical Habitat)
- (E) Winter Run (and Critical Habitat)

(T&E) Steelhead Trout (and Proposed Critical Habitat and Critical Habitat)
- (PT) Northern CA ESU
- (T) Central CA Coast ESU (and Critical Habitat)
- (T) Central Valley ESU (and Critical Habitat)
- (T) South Central CA Coast ESU (and Critical Habitat)
- (E) Southern CA ESU (and Critical Habitat)

(T) Little Kern Golden Trout (and Critical Habitat)
(T) Paiute Cutthroat Trout
(T) Lahonton Cutthroat Trout
(E) Bonytail Chub (and Critical Habitat)
(E) Unarmored Threespine Stickleback (and Proposed Critical Habitat)
(E) Shortnose Sucker (and Proposed Critical Habitat)
(E) Lost River Sucker (and Proposed Critical Habitat)
(T) Sacramento Splittail

Mammals:
(T) Southern Sea Otter