

Group A Elements: Project Management

Element 1. Title and Approval Sheets

QUALITY ASSURANCE PROJECT PLAN

**INCORPORATING WILDLIFE
METHYLMERCURY EXPOSURE AND RISK
ESTIMATES USING BIOMAGNIFICATION
FACTORS INTO CALIFORNIA LAKE
MONITORING**

The Bioaccumulation Oversight Group (BOG)

Surface Water Ambient Monitoring Program

April 2012

Program Title	SWAMP Bioaccumulation Oversight Group Wildlife BMF Study	
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Effective Date	This Quality Assurance Project Plan (QAPP) is effective from April 2012 to May 2013 unless otherwise revised, approved and distributed accordingly at an earlier date.	
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QAPP Preface

This Quality Assurance Project Plan (QAPP) document defines procedures and criteria that will be used for this project conducted by SWAMP Bioaccumulation Oversight Group (BOG) in association with the US Geological Survey (USGS), California Department of Fish and Game Marine Pollution Studies Laboratory (MPSL-DFG), and the San Francisco Estuary Institute (SFEI). Included are criteria for data quality acceptability, procedures for sampling, testing (including deviations) and calibration, as well as preventative and corrective measures. The responsibilities of USGS, MPSL-DFG, and SFEI also are contained within. The BOG selects the sampling sites, the types and size of tissue samples, and the number of analyses to be conducted.

This work is funded through the Surface Water Ambient Monitoring Program (SWAMP) fiscal year 11/12 Bioaccumulation funding.

Approvals

The approvals below were submitted separately, preventing their inclusion in this signature block. Instead, they appear in Appendix VI of this document. Originals are kept on file by Autumn Bonnema of MPSL-DFG.

Rusty Fairey
Contract Manager

_____ Date _____

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Principal Investigator

_____ Date _____

Collin Eagles-Smith
Co-Principal Investigator

_____ Date _____

Jay Davis
Lead Scientist

_____ Date _____

Beverly van Buuren
SWAMP Quality Assurance Officer

_____ Date _____

Autumn Bonnema
Project Coordinator/ MPSL-DFG Quality Assurance Officer

_____ Date _____

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Element 3. Distribution List and Contact Information

A copy of this Quality Assurance Project Plan (QAPP), in hardcopy or electronic format, is to be received and retained by at least one person from each participating entity. At least one person from each participating entity (names shown with asterisk*) shall be responsible for receiving, retaining and distributing the QAPP to their respective staff within their own organization. Contact information for the primary contact person (listed first) for each participating organization also is provided below in Table 1.

Table 1. Contact Information

Name	Agency, Company or Organization
<u>SAN FRANCISCO ESTUARY INSTITUTE</u>	
Jay Davis*	SFEI 7770 Pardee Lane Oakland, CA 94621-1424 Phone: (415) 746-7368 Email: jay@sfei.org
<u>UNITED STATES GEOLOGICAL SURVEY, Forest and Rangeland Ecosystem Science Center</u>	
Collin Eagles-Smith	USGS
Branden Johnson*	3200 SW Jefferson Way Corvallis, OR Phone: (541) 750-0949 Email: ceagles-smith@usgs.gov
<u>UNITED STATES GEOLOGICAL SURVEY, Western Ecological Research Center</u>	
Josh Ackerman	USGS
Alex Hartman	1 Shields Avenue, UC Davis
Robin Keister*	Davis, CA 95616 Phone: (530) 752-0485 Email: jackermad@usgs.gov
<u>MARINE POLLUTION STUDIES LAB</u>	
<u>CALIFORNIA DEPARTMENT OF FISH AND GAME</u>	
Autumn Bonnema*	MPSL-DFG
Dylan Service	7544 Sandholdt Road Moss Landing, CA 95039 Phone: (831) 771-4177 Email: mstephenson@mlml.calstate.edu
<u>MOSS LANDING MARINE LABORATORIES</u>	
<u>QUALITY ASSURANCE RESEARCH GROUP</u>	
Beverly van Buuren*	QA Research Group, MLML
Eric von der Geest	c/o: 4320 Baker Ave. NW Seattle, WA 98107 Phone: (206) 297-1378 Email: bvanbuuren@mlml.calstate.edu

* Indicates person responsible for receiving, retaining, and distributing the final QAPP to staff within their organization

Element 4. Project Organization

The lines of communication between the participating entities, project organization and responsibilities are outlined in Table 2 and Figure 1.

Table 2. Positions and duties

Position	Name	Responsibilities
Contract Manager	Rusty Fairey MPSL-MLML	Approve reports and invoices for payment.
Principal Investigator	Josh Ackerman USGS WERC	
Co-Principal Investigator	Collin Eagles-Smith USGS FRESC Tom Maurer USFWS	
Project Manager	Mark Stephenson MPSL-DFG	Project management and oversight.
Lead Scientist	Jay Davis SFEI	Advisory Roll; Data reporting
Project Coordinator	Autumn Bonnema, MPSL-DFG	Generation of a QAPP, Project coordination; ensures all laboratory activities are completed within proper timeframes.
Program QA Officer	Beverly van Buuren QA Research Group, MLML	Approve QAPP and oversee SWAMP projects' QA/QC
Laboratory QA Officer	Mark Herzog USGS WERC Branden Johnson USGS FRESC Autumn Bonnema, MPSL-DFG	Ensures that the laboratory quality assurance plan and quality assurance project plan criteria are met through routine monitoring and auditing of the systems. Ensure that data meets project's objective through verification of results.
Sample Collection Coordinator	Josh Ackerman USGS WERC Collin Eagles-Smith USGS FRESC Billy Jakl MPSL-DFG	Sampling coordination, operations, and implementing field-sampling procedures.
Laboratory Director	Wes Heim MPSL-DFG	Organizing, coordinating, planning and designing research projects and supervising laboratory staff; Data validation, management and reporting
Sample Custodian	Tully Rohrer USGS Stephen Martenuk MPSL-DFG additional staff	Sample storage. Not responsible for any deliverables.
Technicians	Technical staff USGS MPSL-DFG	Conduct tissue dissection, digestion, and chemical analyses. Responsible for chemistry data submission

4.1. Involved parties and roles

Rusty Fairey of Marine Pollution Studies Lab - Moss Landing Marine Laboratories (MPSL-MLML) will be the Contract Manager (CM) for this project. The CM will approve reports and invoices for payment.

Josh Ackerman of USGS WERC will serve as the Principal Investigator (PI) for this project. The PI

Collin Eagles-Smith (USGS FRESC) and Tom Maurer (USFWS) will serve as Co-Principal Investigators (CPI) for the project.

Mark Stephenson of MPSL-DFG will serve as the Project Manager (PM) for the project. The PM will 1) review and approve the QAPP, 2) review, evaluate and document project reports, and 3) verify the completeness of all tasks.

Jay Davis of San Francisco Estuary Institute (SFEI) is the Lead Scientist (LS) and primary contact of this project. The LS will 1) generate the Sampling and Analysis Plan (SAP), 2) approve the QAPP, and 3) provide the BOG with a final report on completion of this project.

Autumn Bonnema of MPSL-DFG is the Project Coordinator (PC). The PC will 1) prepare the QAPP, 2) ensure that laboratory technicians have processing instructions and 3) ensure all laboratory activities are completed within the proper timelines. In addition, the PC may assist field crew in preparation and logistics.

Dylan Service of MPSL-DFG is in charge of directing fish collection for this project. He will 1) oversee preparation for sampling, including vehicle maintenance and 2) oversee sample and field data collection.

Collin Eagles-Smith and Josh Ackerman are in charge of directing grebe tissue collections for this project. They will 1) oversee preparation for sampling, including vehicle maintenance and 2) oversee sample and field data collection.

Stephen Martenuk is responsible for sample storage and custody at MPSL. His duties will be to oversee compositing of tissue samples. Tully Rohrer will do the same for samples processed at USGS.

Collin Eagles-Smith and Josh Ackerman will serve as the Laboratory Directors (LD) for the USGS component of this project. Their specific duties will be to 1) review and approve the QAPP, 2) provide oversight for mercury analyses on grebe tissues to be done for this project, and 3) ensure that all USGS activities are completed within the proper timelines.

Wes Heim will also serve as the Laboratory Director (LD) for the MPSL-DFG component of this project. His specific duties will be to 1) review and approve the QAPP, 2) provide oversight

for mercury analyses on fish tissues to be done for this project, and 3) ensure that all MPSSL-DFG activities are completed within the proper timelines.

The following serve in an advisory role and are not responsible for any deliverables: Terry Fleming (EPA), Bob Brodberg (Office of Environmental Health Hazard Assessment (OEHHA)), Karen Taberski (RWQCB2), Mary Hamilton (RWQCB3), Michael Lyons (RWQCB4), Chris Foe (RWQCB5), Cassandra Lamerdin (MPSSL-MLML), Jennifer Salisbury (State Water Resources Control Board (SWRCB)), Gary Ichikawa (Department of Fish and Game), Dylan Service (MPSSL-DFG), Alex Hartman (USGS) and Jennifer Hunt (SFEI).

4.2. Quality Assurance Officer (QAO) Role

The Laboratory Quality Assurance Officers fulfill the functions and authority of a project quality assurance officer (QAO). Autumn Bonnema is the MPSSL-DFG QAO, Mark Herzog is the USGS WERC QAO, and Branden Johnson is the USGS FRESC QAO. The role of the Laboratory QAO is to ensure that quality control for sample processing and data analysis procedures described in this QAPP are maintained throughout the project. The Program QAO (Beverly van Buuren, MLML) acts in a consulting role to the Laboratory QAOs and ensures the project meets all SWAMP QA/QC criteria (QAPrP, 2008).

The Laboratory QAOs will review and assess all procedures during the life of this project against QAPP requirements, and assess whether the procedures are performed according to protocol. The Laboratory QAOs will report all findings (including qualified data) to the Program QAO and the PM, including all requests for corrective action. The Laboratory and Program QAOs have the authority to stop all actions if there are significant deviations from required procedures or evidence of a systematic failure.

A conflict of interest does not exist between the Laboratory QAOs and the work outlined in this QAPP as neither Laboratory QAO participates in any of the chemical analyses of the project. There is not a conflict of interest with one person fulfilling the roles of Laboratory QAO and Project Coordinator (PC), as laboratory decisions are not made by the PC and no other duties overlap. The role of the PC is detailed above.

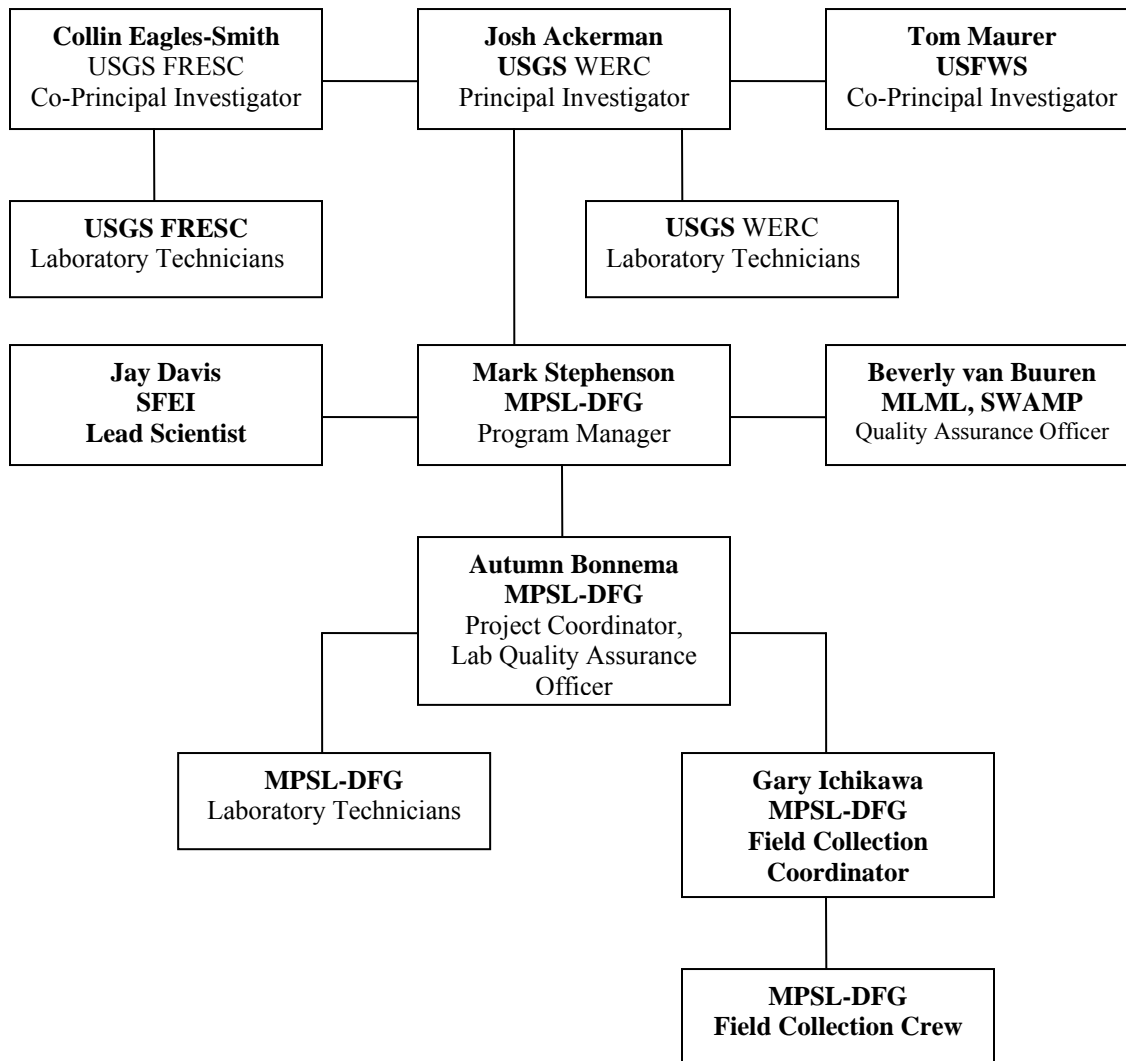
4.3. Persons responsible for QAPP update and maintenance

Revisions and updates to this QAPP will be carried out by Autumn Bonnema (PC), with technical input of the PM and the Laboratory and Program QAOs. All changes will be considered draft until reviewed and approved by the PM and the SWAMP QAO. Finalized revisions will be submitted for approval to the SWAMP QAO, if necessary.

Copies of this QAPP will be distributed to all parties involved in the project. Any future amended QAPPs will be held and distributed in the same fashion. All originals of these first and subsequent amended QAPPs will be held on site at SFEI, USGS and MPSSL-DFG.

4.4. Organizational chart and responsibilities

Figure 1. Organizational Chart



Element 5. Problem Definition/Background

5.1. Problem statement

5.1.1. Addressing Multiple Beneficial Uses

Bioaccumulation in California water bodies has an adverse impact on both the fishing and aquatic life beneficial uses (Davis et al. 2007). The fishing beneficial use is affected by human exposure to bioaccumulative contaminants through consumption of sport fish. The aquatic life beneficial use is affected by exposure of wildlife to bioaccumulative contaminants, primarily piscivorous species exposed through consumption of small fish. Different indicators are used to monitor these different types of exposure. Monitoring of status and trends in human exposure is accomplished through sampling and analyzing sport fish. On the other hand, monitoring of status and trends in wildlife exposure can be accomplished through sampling and analysis of wildlife prey (small fish, other prey species) or tissues of the species of concern (e.g., bird eggs or other tissues of juvenile or adults of the species at risk).

The Surface Water Ambient Monitoring Program (SWAMP) via the Bioaccumulation Oversight Group (BOG) has recently completed state-wide surveys of contaminants in sport fish tissue from over 250 lakes in California and throughout coastal waters. However, this impressive effort only focused on human health issues. Because many fish-eating wildlife such as grebes, terns, cormorants, and mergansers eat fish smaller than those that were sampled by BOG, and since fish mercury concentrations are not always indicative of wildlife exposure to mercury, the current BOG surveys do not address whether wildlife beneficial uses may be impaired by mercury in these water bodies.

5.1.2. Addressing Multiple Monitoring Objectives and Assessment Questions for Aquatic Life Beneficial Uses

The BOG has developed a set of monitoring objectives and assessment questions for a statewide program evaluating the impacts of bioaccumulation on the fishing beneficial use. This assessment framework is consistent with frameworks developed for other components of SWAMP, and is intended to guide the bioaccumulation monitoring program over the long-term. The four objectives can be summarized as 1) status; 2) trends; 3) sources and pathways; and 4) effectiveness of management actions.

Over the long-term, the primary emphasis of the statewide bioaccumulation monitoring program will be on evaluating status and trends. Bioaccumulation monitoring is a very effective and essential tool for evaluating status, and is most cost-effective tool for evaluating trends for many contaminants. Monitoring status and trends in bioaccumulation will provide some information on sources and pathways and effectiveness of management actions at a broader geographic scale. However, other types of monitoring (i.e., water and sediment monitoring) and other programs (regional TMDL programs) are also needed for addressing sources and pathways and effectiveness of management actions.

In the near-term, the primary emphasis of the statewide bioaccumulation monitoring program will be on evaluating Objective 1 (status). The reasons for this are:

1. a systematic statewide assessment of status has never been performed and is urgently needed;
2. we are starting a new program and establishing a foundation for future assessments of trends;
3. past monitoring of sport fish established very few time series that are useful in trend analysis that this program could have built upon.

5.1.3. Addressing Multiple Habitat Types

SWAMP has defined the following categories of water bodies:

- lakes and reservoirs;
- bays and estuaries;
- coastal waters;
- large rivers;
- wadeable streams; and
- wetlands.

Due to their vast number, high fishing pressure, and a relative lack of information on bioaccumulation (Davis et al. 2007), lakes and reservoirs were identified as the first priority for sport fish monitoring. Coastal waters, including bays and estuaries, were selected as the next priority, due to their importance for sport fishing and a relative lack of past monitoring. Rivers and streams were the last in the series of water body types to be covered with a statewide screening study. Wetlands were not covered due to the low fishing pressure in those habitats.

Following the sequence established for the fishing beneficial use, assessment of the impact of bioaccumulation on aquatic life beneficial uses is also beginning with a focus on lakes and reservoirs. Methylmercury exposure and risk was identified as the greatest concern in this habitat type, and reproduction in piscivorous birds as the taxa and lifestage at greatest risk. The logistics of performing surveys of exposure and risk in wildlife, require much greater effort and time at each water body, and thus do not readily allow for statewide surveys of the same breadth as were performed for sport fish. However, a two-year study covering 24 lakes was considered to be feasible within the scope of available funding and staffing, and is expected to be sufficient to answer some critical general questions with regard to aquatic life beneficial uses. Including other contaminants or habitats is not feasible with existing funding at this time.

Bioaccumulation is likely having negative impacts on aquatic life beneficial uses in all of the habitat types identified by SWAMP, including wetlands, which are among the most important habitats for wildlife. Whether SWAMP will perform surveys in the other habitat types has not yet been determined. The results of this preliminary assessment of methylmercury impacts in lakes and reservoirs will be valuable in informing the decision on the priority of further assessments.

In summary, focusing on one habitat type (lakes and reservoirs), one objective (status), and one category of beneficial use (aquatic life) will allow us to provide reasonable coverage and provide an informative assessment of bioaccumulation in these habitats in a two-year study.

5.2. Decisions or outcomes

In response to information needs articulated by the state and regional Water Boards, three management questions have been articulated to guide the 2012 screening survey of the status of bioaccumulation in wildlife in California Lakes. Questions relating to 303(d) listing (included in the lakes survey) and spatial patterns (included in the coast survey) were not a priority for managers and were not included in this survey.

5.2.1. Management Question 1 (MQ1)

Does methylmercury pose significant risks to aquatic life in a representative sample of California lakes and reservoirs?

Answering this question is critical to determining the degree of impairment of the wildlife beneficial use across the state due to bioaccumulation. This question places emphasis on characterizing the status of the wildlife beneficial use through monitoring of wildlife and prey fish exposure. A systematic statewide survey of wildlife risk to Hg in freshwater lakes has never been performed.

The data needed to answer this question are average Hg concentrations in Western grebe blood and eggs, and prey fish from various lakes throughout California. Western grebes are useful wildlife indicators for this task because they breed widely throughout California, are upper-trophic level fish-eating birds, and are flightless during breeding, making their Hg concentrations reflective of conditions within individual lakes. Monitoring species that accumulate high concentrations of contaminants (“indicator species”) is valuable in answering this question: if concentrations in these species are below thresholds, this is a strong indication that an area has low concentrations.

5.2.2. Management Question 2 (MQ2)

Can a biomagnification factor approach be applied on a statewide basis to estimate risks to birds based on concentrations measured in small fish?

The Surface Water Ambient Monitoring Program (SWAMP) via the Bioaccumulation Oversight Group (BOG) has recently completed state-wide surveys of contaminants in sport fish tissue from over 250 lakes in California and throughout coastal waters. However, this impressive effort only focused on human health issues. Because many fish-eating wildlife such as grebes, terns, cormorants, and mergansers eat fish smaller than those that were sampled by BOG, and since fish mercury concentrations are not always indicative of wildlife exposure to mercury, the current BOG surveys do not address whether wildlife beneficial uses may be impaired by mercury in these water bodies.

When properly derived, biomagnification factors are valuable because they provide managers and regulators with a quantitative tool to estimate mercury concentrations across environmental

matrices, thus enabling them to adequately estimate wildlife exposure without the need for comprehensive sampling at all sites of interest. Biomagnification factors (BMF) are derived for biota from the organism's diet, and are calculated by dividing the chemical concentration in the predator by the chemical concentration in the predator's diet. This biomagnification factor can then be used for translating small fish mercury concentrations to bird mercury concentrations.

5.2.3. Management Question 3 (MQ3)

What are appropriate TMDL monitoring requirements to address methylmercury exposure in wildlife?

Understanding the transferability of biomagnification factors across lakes and species will be important for understanding whether small or large fish provide a useful index of wildlife exposure. The approach used here will test whether a single, broad translator adequately captures wildlife risk, or if region or lake specific coefficients are needed.

5.2.4. Overall Approach

To answer these questions, over two consecutive field seasons in 2012 and 2013, we will sample birds and small fish simultaneously at 24 lakes throughout California during the breeding season when birds are particularly vulnerable to potential mercury-induced reproductive impairment. Specifically, the study will have four main components:

- 1) Sample grebes at 24 California lakes over 2 years to determine mercury levels in a species near the top of the food chain, and compare these data to known effects-thresholds for birds.
- 2) Simultaneously with grebe sampling, collect small fish (<100 mm) at these same 24 lakes over 2 years to determine if mercury concentrations are above current wildlife diet objectives.
- 3) Use these data in Objectives 1 and 2 to calculate a bird biomagnification factor, evaluate the biomagnification factor's usefulness for estimating wildlife exposure, and assess whether the biomagnification factor differs by lake type or geographic region.

Simultaneously with grebe and small fish sampling, collect sport fish at these same 24 lakes over 2 years to assess correlations of mercury concentrations in sport fish, small fish, and birds

5.2.5. Coordination

The BOG is seeking to coordinate with other programs to leverage the funds for this survey and achieve more thorough studies relating to bioaccumulation in California lakes.

One significant collaboration will be with the US Geological Survey (USGS). The USGS will be collecting and analyzing the grebe tissues, as well as writing the report on that portion of the study. Furthermore, they are contributing approximately \$96,000 in In-Kind funds.

5.3. Tissue contamination criteria

Determination of effects-thresholds in wildlife species is complicated by variation in species sensitivity. However, extensive work on common loons in eastern North America suggest that

toxic effects become measurable and reproduction is impaired at blood concentrations of 3 ug/g wet weight or greater (Evers et al. 2007). Those values also relate to egg concentrations of approximately 1.8 ug/g wet weight (Evers et al. 2003).

A small fish criterion is presently in development by the State Board. However, it is not certain that this criterion will be available in time for the reporting of the results of the first year of this study. When the criterion does become available, results from this study will be assessed in comparison to this threshold.

Threshold levels for determining impairment of a body of water based on pollutants in fish tissue are listed in Table 3. Fish Contaminant Goals (FCGs), as described by Klasing and Brodberg (2008), are “estimates of contaminant levels in fish that pose no significant health risk to humans consuming sport fish at a standard consumption rate of one serving per week (or eight ounces [before cooking] per week, or 32 g/day), prior to cooking, over a lifetime and can provide a starting point for OEHHA to assist other agencies that wish to develop fish tissue-based criteria with a goal toward pollution mitigation or elimination. FCGs prevent consumers from being exposed to more than the daily reference dose for non-carcinogens or to a risk level greater than 1×10^{-6} for carcinogens (not more than one additional cancer case in a population of 1,000,000 people consuming fish at the given consumption rate over a lifetime). FCGs are based solely on public health considerations without regard to economic considerations, technical feasibility, or the counterbalancing benefits of fish consumption.” For organic pollutants, FCGs are lower than Advisory Tissue Levels (ATL)s.

ATLs, as described by Klasing and Brodberg (2008), “while still conferring no significant health risk to individuals consuming sport fish in the quantities shown over a lifetime, were developed with the recognition that there are unique health benefits associated with fish consumption and that the advisory process should be expanded beyond a simple risk paradigm in order to best promote the overall health of the fish consumer. ATLs provide numbers of recommended fish servings that correspond to the range of contaminant concentrations found in fish and are used to provide consumption advice to prevent consumers from being exposed to more than the average daily reference dose for non-carcinogens or to a risk level greater than 1×10^{-4} for carcinogens (not more than one additional cancer case in a population of 10,000 people consuming fish at the given consumption rate over a lifetime). ATLs are designed to encourage consumption of fish that can be eaten in quantities likely to provide significant health benefits, while discouraging consumption of fish that, because of contaminant concentrations, should not be eaten or cannot be eaten in amounts recommended for improving overall health (eight ounces total, prior to cooking, per week). ATLs are but one component of a complex process of data evaluation and interpretation used by OEHHA in the assessment and communication of fish consumption risks. The nature of the contaminant data or omega-3 fatty acid concentrations in a given species in a water body, as well as risk communication needs, may alter strict application of ATLs when developing site-specific advisories. For example, OEHHA may recommend that consumers eat fish containing low levels of omega-3 fatty acids less often than Table 3 would suggest based solely on contaminant concentrations. OEHHA uses ATLs as a framework, along with best professional judgment, to provide fish consumption guidance on an ad hoc basis that best combines the needs for health protection and ease of communication for each site.”

Table 3. Sport fish assessment thresholds

Thresholds for concern based on an assessment of human health risk from these pollutants by OEHHA (Klasing and Brodberg, 2008). All values given in ng/g (ppb). The lowest available threshold for each pollutant is in bold font. One serving is defined as 8 ounces (227 g) prior to cooking. The FCG and ATs for mercury are for the most sensitive population (i.e., women aged 18 to 45 years and children aged 1 to 17 years).

Pollutant	Fish Contaminant Goal	Advisory Tissue Level (3 servings/week)	Advisory Tissue Level (2 servings/week)	Advisory Tissue Level (No Consumption)
Chlordanes	5.6	190	280	560
DDTs	21	520	1000	2100
Dieldrin	0.46	15	23	46
Mercury	220	70	150	440
PCBs	3.6	21	42	120
Selenium	7400	2500	4900	15000

Element 6. Project Description

6.1. Work statement and produced products

This study will be completed in two years of sampling. Sampling will focus on the California lakes known to support grebe breeding with primary focus on those lakes previously studied under the 2 year BOG Lakes study. Chemistry and ancillary data will be collected from fish caught at these sites, and a report of the findings will be made publicly available in 2013.

6.2. Constituents to be analyzed and measurement techniques.

A detailed Sampling and Analysis Plan (SAP) is in Appendix II. Chemistry analytical methods are summarized in Section E. Constituents to be analyzed are summarized in Tables 4-6. All chemistry data will be reported on a wet weight basis. Analytical methods are listed in each table as appropriate.

Table 4. Constituents to be Analyzed – Grebe Attributes

Grebe Attributes
Body Mass (g)
Flattened wing chord (mm)
Tarsus length (mm)
Exposed culmen length (mm)
Moisture (%)
Collection Location (UTMs)

Table 5. Constituents to be Analyzed – Fish Attributes

Fish attributes are physical measurements or observations. These are not covered in any analytical method.

Fish Attributes
Total Length (mm)
Fork Length (mm)
Weight (g)
Sex (sport fish only)
Moisture (%)
Collection Location (UTMs)

Table 6. Constituents to be Analyzed – Metals and Metalloids

Analyte	Tissue Type	Analytical Method
Total Mercury	Grebe blood and eggs	EPA 7473 (USEPA 1998)
Total Mercury	Whole Body Small Fish and Sport muscle	EPA 7473 (USEPA 1998)

6.3. Project schedule and number of samples to be analyzed.

Key tasks in the project and their expected due dates are outlined in Table 7.

Table 7. Project Schedule Timeline

Item	Activity and/or Deliverable	Deliverable Due Date
1	Contracts	
	Subcontract Development	February 2012
2	Quality Assurance Project Plan & Monitoring Plan	
2.1	Draft Monitoring Plan	February 2012
2.2	Final Monitoring Plan	March 2012
2.3	Draft Quality Assurance Project Plan	April 2012
2.4	Final Quality Assurance Project Plan	May 2012
3	Sample Collection	Year 1 April-October 2012 Year 2 April-October 2013
4	Sample Selection and Chemical Analysis	
4.1	Selection of Tissue for Analysis	Year 1 September-October 2012 Year 2 September-October 2013
4.2	Creation of Sample Composites	Year 1 October-November 2012 Year 2 October-November 2013
4.3	Chemical Analysis	Year 1 November 2012-February 2013 Year 2 November 2013-February 2014
4.4	Small Fish Data Reported to SWAMP	Year 1 March 2013 Year 2 March 2014
4.4	Grebe Data Reported to CEDEN	Year 1 May 2013 Year 2 May 2014
5	Data Quality Assessment and Narrative	Year 1 May 2013 Year 2 May 2013
6	Interpretive Report	
6.1	Draft Report	Year 1 March 2014 Year 2 March 2015
6.2	Final Report	Year 1 May 2013 Year 2 May 2014

6.4. Geographical setting and sample sites

Sampling will occur in freshwater lakes throughout California that contain breeding grebe colonies. Site selection and timing will be determined based on breeding grebe locations and relative abundance of grebes. See the Proposal and Study Plan for a map depicted primary and alternate sampling lakes.

6.5. Constraints

All sampling must be completed by the end of the current year's sampling season in order to meet analysis and reporting deadlines set forth in Table 7.

Element 7. Quality Indicators and Acceptability Criteria for Measurement Data

Data quality indicators for the analysis of grebe and fish tissue mercury concentrations will include accuracy (bias), precision, recovery, completeness and sensitivity. Measurement Quality Indicators for analytical measurements in tissue are in Table 8.

Previously collected data will not be utilized in this study, therefore specific acceptance criteria are not applicable.

Table 8. Measurement quality indicators for laboratory measurements.

Parameter	Accuracy	Precision	Recovery	Completeness	Sensitivity
Trace metals (including mercury)	CRM 75% - 125%	Duplicate RPD <25%; n/a if concentration of either sample <RL Matrix Spike Duplicate RPD <25%	Matrix Spike 75% - 125%	90%	See Table 12

7.1. Accuracy

Evaluation of the accuracy of laboratory procedures is achieved through the preparation and analysis of reference materials with each analytical batch. Ideally, the reference materials selected are similar in matrix and concentration range to the samples being prepared and analyzed. The accuracy of the results is assessed through the calculation of a percent recovery.

$$\% \text{ recovery} = \frac{V_{\text{analyzed}}}{V_{\text{certified}}} \times 100$$

Where:

V_{analyzed} : the analyzed concentration of the reference material

$V_{\text{certified}}$: the certified concentration of the reference material

The acceptance criteria for reference materials are listed in Table 9.

Table 9. Measurement Quality Objectives – Inorganic Analytes in Tissues

SWAMP Measurement Quality Objectives* - General		
Laboratory Quality Control	Frequency of Analysis	Measurement Quality Objective
Calibration Standard	Per analytical method or manufacturer's specifications	Per analytical method or manufacturer's specifications
Continuing Calibration Verification	Per 10 analytical runs	80-120% recovery
Laboratory Blank	Per 20 samples or per batch, whichever is more frequent	<RL for target analyte
Reference Material	Per 20 samples or per batch, whichever is more frequent	75-125% recovery
Matrix Spike	Per 20 samples or per batch, whichever is more frequent	75-125% recovery
Matrix Spike Duplicate	Per 20 samples or per batch, whichever is more frequent	75-125% recovery, RPD ≤25%
Laboratory Duplicate	Per 20 samples or per batch, whichever is more frequent	RPD <25%; n/a if concentration of either sample <MDL
Internal Standard	Accompanying every analytical run when method appropriate	75-125% recovery

*Unless method specifies more stringent requirements.

MDL = Method Detection Limit

RL = Reporting Limit

n/a = not applicable

7.2. Precision

In order to evaluate the precision of an analytical process, a field sample is selected and digested or extracted in duplicate. Following analysis, the results from the duplicate samples are evaluated by calculating the Relative Percent Difference (RPD).

$$RPD = \left| \frac{(V_{\text{sample}} - V_{\text{duplicate}})}{\text{mean}} \right| \times 100$$

Where:

V_{sample} : the concentration of the original sample digest

$V_{\text{duplicate}}$: the concentration of the duplicate sample digest
mean: the mean concentration of both sample digests

The acceptance criteria for laboratory duplicates are specified in Table 9.

A minimum of one duplicate per analytical batch will be analyzed. If the analytical precision is unacceptable, calculations and instruments will be checked. A repeat analysis may be required to confirm the results.

Duplicate precision is considered acceptable if the resulting RPD is $\leq 25\%$ for analyte concentrations that are greater than the Minimum Level (ML). The U.S. Environmental Protection Agency (EPA) defines the ML as the lowest level at which the entire analytical system must give a recognizable signal and acceptable calibration point for the analyte. It is equivalent to the concentration of the lowest calibration standard, assuming that all standard operating procedure (SOP) or method-specified sample weights, volumes, and cleanup procedures have been employed.

7.2.1. Replicate Analysis

Replicate analyses are distinguished from duplicate analyses based simply on the number of involved analyses. Duplicate analyses refer to two sample digests, while replicate analyses refer to three or more. Analysis of replicate samples is not explicitly required; however it is important to establish a consistent method of evaluating these analyses. The method of evaluating replicate analysis is by calculation of the relative standard deviation (RSD). Expressed as a percentage, the RSD is calculated as follows:

$$\text{RSD} = \frac{\text{Stdev}(v_1, v_2, \dots, v_n)}{\text{mean}} \times 100$$

Where:

Stdev(v_1, v_2, \dots, v_n): the standard deviation of the values (concentrations) of the replicate analyses.

mean: the mean of the values (concentrations) of the replicate analyses.

7.3. Bias

Bias is the systematic or persistent distortion of a measurement process that skews data in one direction. Certified Reference Materials (CRM) and Matrix Spike (MS) samples are used to determine the analyte-specific bias associated with each analytical laboratory. CRMs are used to determine analytical bias, and MS are used to determine the bias associated with the tissue matrix.

A matrix spike (MS) is prepared by adding a known concentration of the target analyte to a field sample, which is then subjected to the entire analytical procedure. If the ambient concentration of the field sample is known, the amount of spike added is within a specified range of that concentration. Matrix spikes are analyzed in order to assess the magnitude of matrix interference and bias present. Because matrix spikes are analyzed in pairs, the second spike is called the matrix spike duplicate (MSD). The MSD provides information regarding the precision of the matrix effects. Both the MS and MSD are split from the same original field sample.

The success or failure of the matrix spikes is evaluated by calculating the percent recovery.

$$\% \text{ recovery} = \frac{(V_{\text{MS}} - V_{\text{ambient}})}{V_{\text{spike}}} \times 100$$

Where:

- V_{MS} : the concentration of the spiked sample
- $V_{ambient}$: the concentration of the original (unspiked) sample
- V_{spike} : the concentration of the spike added

In order to properly assess the degree of matrix interference and potential bias, the spiking level should be approximately 2-5 times the ambient concentration of the spiked sample but at least 3 times the reporting limit. If the MS or MSD is spiked too high or too low relative to the ambient concentration, the calculated recoveries are no longer an acceptable assessment of analytical bias. In order to establish spiking levels prior to analysis of samples, the laboratories should review any relevant historical data. In many instances, the laboratory will be spiking the samples blind and will not meet a spiking level of 2-5 times the ambient concentration. However, the results of affected samples will not be automatically rejected.

In addition to the recoveries, the RPD between the MS and MSD is calculated to evaluate how matrix affects precision.

$$RPD = \left| \frac{(V_{MS} - V_{MSD})}{\text{mean}} \right| \times 100$$

There are two different ways to calculate this RPD, depending on how the samples are spiked.

- 1) The samples are spiked with the same amount of analyte. In this case,
 - V_{MS} : the concentration for the matrix spike
 - V_{MSD} : the concentration of the matrix spike duplicate mean: the mean of the two concentrations (MS + MSD)
- 2) The samples are spiked with different amounts of analyte. In this case,
 - V_{MS} : the recovery associated with the matrix spike
 - V_{MSD} : the recovery associated with matrix spike duplicate mean: the mean of the two recoveries ($\text{recovery}_{MS} + \text{recovery}_{MSD}$)

The MQO for the RPD between the MS and MSD is the same regardless of the method of calculation; detailed in Table 9.

7.4. Contamination assessment – Method blanks

Laboratory method blanks (also called extraction blanks, procedural blanks, or preparation blanks) are used to assess laboratory contamination during all stages of sample preparation and analysis. At least one laboratory method blank will be run in every sample batch of 20 or fewer field samples. The method blanks will be processed through the entire analytical procedure in a manner identical to the samples. The QC criterion for method blank analysis states that the blanks must be less than the Reporting Limit (<RL) for target analytes. If blank values exceed the RL, the sources of the contamination are determined and corrected, and in the case of method blanks, the previous samples associated with the blank are re-analyzed. All blank analysis results will be reported. If it is not possible to eliminate the contamination source, all impacted analytes in the analytical batch will be flagged. In addition, a detailed description of the

contamination sources and the steps taken to eliminate/minimize the contaminants will be included in interim and final reports. Subtracting method blank results from sample results is not permitted, unless specified in the analytical method.

7.8. Representativeness

The representativeness of the data is mainly dependent on the sampling locations and the sampling procedures adequately representing the true condition of the sample site. Requirements for selecting sample sites are discussed in more detail in the SAP (Appendix II). Sample site selection, sampling of relevant media (water, sediment and biota), and use of only approved/documented analytical methods will determine that the measurement data does represent the conditions at the investigation site, to the extent possible.

7.9. Completeness

Completeness is defined as “a measure of the amount of data collected from a measurement process compared to the amount that was expected to be obtained under the conditions of measurement” (Stanley and Verner, 1985).

Field personnel will always strive to achieve or exceed the SWAMP completeness goals of 90% for fish samples when target species (SAP Table 1 Appendix II) are present. Due to the variability and uncertainty of species availability in each zone, this level of completeness may not be attainable. If grebes or fish cannot be collected from a particular location, another location may be chosen to replace it. Additional locations will be chosen by the PI with input from Regional Board staff. Additionally, colony size may limit grebe egg collection in some areas. In order to generate the most robust data necessary, any lakes where targeted egg collections are not possible the PIs will collect grebe feathers as the 2nd tissue for analysis.

In the event field documentation is incomplete, datasheets will be returned to the collection crew for amendment.

Laboratories will strive for analytical completeness of 90% (Table 8). In the event laboratory documentation is incomplete, datasheets will be returned to the dissector for amendment.

Occasionally digestates or extracts are rendered unusable for various reasons in the preparation process. If this occurs, the sample(s) affected will be re-processed.

Element 8. Special Training Requirements/Safety

8.1. Specialized training and safety requirements

Analysts are trained to conduct a wide variety of activities using standard protocols to ensure samples are analyzed in a consistent manner. Training of each analyst includes the use of analytical equipment and conducting analytical protocols, and other general laboratory processes including glassware cleaning, sampling preparation and processing, hazardous materials

handling, storage, disposal. All laboratory staff must demonstrate proficiency in all the aforementioned and required laboratory activities that are conducted, as certified by the Laboratory QAO.

8.2. Training, safety and certification documentation

Staff and safety training is documented at USGS and MPSL-DFG. Documentation consists of a record of the training date, instructor and signatures of completion. The Laboratory QAO will certify the proficiency of staff at chemical analyses. Certification and records are maintained and updated by the Laboratory QAO, or their designee, for all laboratory staff.

8.3. Training personnel

The USGS or MPSL-DFG Lab Director (LD) trains or appoints senior staff to train personnel. The Laboratory QAO ensures that training is given according to standard laboratory methods, maintains documentation and performs performance audits to ensure that personnel have been trained properly.

8.3.1. Laboratory Safety

New laboratory employees receive training in laboratory safety and chemical hygiene prior to performing any tasks in the laboratory. Employees are required to review the laboratory's safety program and chemical hygiene plan and acknowledge that they have read and understood the training. An experienced laboratory employee or the laboratory safety officer is assigned to the new employee to provide additional information and answer any questions related to safety that the new employee may have.

On-going safety training is provided by quarterly safety meetings conducted by the laboratory's safety officer or an annual laboratory safety class conducted by the USGS Safety Officers or MLML Chemical Safety Officer.

8.3.2. Technical Training

New employees and employees required to learn new test methods are instructed to thoroughly review the appropriate standard operating procedure(s) and are teamed up with a staff member who is experienced and qualified to teach those test methods and observe and evaluate performance. Employees learning new test methods work with experienced staff until they have demonstrated proficiency for the method both by observation and by obtaining acceptable results for QC samples. This demonstration of proficiency is documented and certified by the section leader, Laboratory QAO and the laboratory director prior to the person independently performing the test method. Training records are retained on file for each employee by their supervisor or QAO. On-going performance is monitored by reviewing QC sample results.

Element 9. Documentation and Records

The following documents, records, and electronic files will be produced:

- Quality Assurance Project Plan (submitted to contract manager in paper and electronic formats)
- Sampling and Analysis Plan (submitted to contract manager in paper and electronic formats)
- Archived Sample Sheets (internal documentation available on request)
- Chain-of-Custody Forms (exchanged for signatures with chemistry lab, and kept on file)
- Lab Sample Disposition Logs (internal documentation available on request)
- Calibration Logs for measurements of water quality standards (internal documentation available on request)
- Refrigerator and Freezer Logs (internal documentation available on request)
- Quarterly Progress Reports (oral format to contract manager)
- Data Tables (submitted to contract manager in electronic formats)
- Draft Manuscript (produced in electronic format)
- Final Manuscript (in electronic format)
- Data Appendix (submitted to contract manager in paper and electronic spreadsheet formats)

Copies of this QAPP will be distributed by the project manager to all parties directly involved in this project. Any future amended QAPPs will be distributed in the same fashion. All originals of the first and subsequent amended QAPPs will be held at MPSL-DFG. Copies of versions, other than the most current, will be discarded to avoid confusion.

The final report will consist of summary data tables and an appendix that contains all project data in electronic SWAMP compatible spreadsheet format. All laboratory logs and data sheets will be maintained at the generating laboratory by the Laboratory Manager for five years following project completion, and are available for review by the Contract Manager or designee during that time. Copies of reports will be maintained at SFEI for five years after project completion then discarded, except for the database, which will be maintained without discarding. Laboratories will provide electronic copies of tabulated analytical data (including associated QA/QC information outlined below) in the SWAMP database format or a format agreed upon by the Contract Manager. All electronic data are stored on computer hard drives and electronic back-up files are created every two weeks or more frequently.

Laboratories will generate records for sample receipt and storage, analyses and reporting.

Laboratories maintain paper copies of all analytical data, field data forms and field notebooks, raw and condensed data for analysis performed on-site, and field instrument calibration notebooks.

The PC will be responsible for sending out the most current electronic copies of the approved QAPP to all appropriate persons listed in Table 1.

Group B Elements. Data Generation and Acquisition

Element 10. Sample Process Design

The project design is described in the Sampling and Analysis Plan (SAP), Section B, pp. 6-8 (Appendix II). Twenty-four lakes and reservoirs identified as western grebe breeding areas will be sampled, where possible, for birds, small fish and sport fish. Effort will first be put into grebe blood and eggs collections. Once suitable samples have been taken, small fish and sport fish collections will commence within 2-3 weeks. It is important not to collect fish before grebe samples, since data on the birds is pivotal to the development of a model.

Potential small fish and sport fish sampling equipment and methods can be found in MPSL-102a (Appendix III). Once samples have been identified for composite creation, they will be processed according to the timeline in Table 7.

All measurements and analyses to be performed are critical to address the objectives laid out in Section III of the SAP (Appendix II), with the exception of grebe parameters, fish weight, sex, and moisture content. These parameters may be used to support other data gathered.

10.1. Variability

The grebe tissue and small fish samples will be analyzed individually as outlined in the SAP (Appendix II) and MPSL-DFG SOPs (Appendix III). Sport fish composites may be created for non-bass species collected because of variability within species.

10.2. Bias

Bias can be introduced by using fish of one particular species and/or total length for chemistry regressions and statistical analyses. The SAP (Appendix II) was reviewed by a Scientific Review Panel which approved of the inclusion of length ranges and multiple target species to reduce the associated bias.

Element 11. Sampling Methods

Grebe tissue samples will be collected in accordance with USGS standard operating procedures. One egg from up to 30 nests (but typically 5-10 eggs) from each breeding colony

will be collected (Egg Collection SOP, Appendix IV A). Blood will be collected via heparinized needles and syringes (Blood Collection SOP, Appendix IV B).

Fish will be collected in accordance with MPSL-102a, Section 7.4 (Appendix III B) except where noted here. Because habitats may vary greatly, there is no one method of collection that is appropriate. Field crews will evaluate each fishing site and species targeted to determine the correct method to be employed. Potential sampling methods include, but are not limited to: electroshocking, seining, gill netting, and hook and line. Field Crew will determine the appropriate collection method based on physical site parameters such as depth, width, flow, and accessibility. Field crew will indicate collection method on data sheets (Attachment 2).

Details on targeted fish species, number of individuals and size ranges can be found in the SAP (Appendix II, Tables 1-2).

The following adaptation to MPSL-102a, Section 7.4.5 (Appendix III) has been made: Collected fish may be partially dissected in the field. At the dock, the fish is placed on a measuring board covered with clean aluminum foil; fork and total length are recorded. Weight is recorded. Large fish such as carp will then be placed on the cutting board covered with a foil where the head, tail, and guts are removed using a clean cleaver (scrubbed with Micro™, rinsed with tap and deionized water). The fish cross section is tagged with a unique numbered ID, wrapped in aluminum foil, and placed in a clean labeled bag. When possible, parasites and body anomalies are noted. The cleaver and cutting board are re-cleaned with Micro™, rinsed with tap and deionized water between fish species, per site if multiple stations are sampled.

Special care is being taken to prevent the potential contamination of invasive species from one location to another. A 10% bleach solution is sprayed on all boat and personal gear components that come into contact with ambient water from each location. In addition, a visual inspection of the boat or equipment is conducted to ensure any algae or other organisms are not transferred between locations. Furthermore, boat bilges are verified to be dry before the boat is launched into a location.

Further details on sample collection and processing can be found in the SAP (Appendix II).

11.1. Corrective Action

In the event samples cannot be collected, the Sample Collection Coordinator will determine if corrective actions are appropriate. Table 10 describes action to take in the event of a collection failure.

Table 10. Field collection corrective actions

Collection Failure	Corrective Action
No Breeding Grebes Present	Inform PC and move on to another location – another location may be substituted; document the occurrence
Egg collection not possible	Collect feathers instead, or increase number of grebe blood samples at that lake
Only one species of small fish present	Collect from that species alone
No sport fish present	Inform PC and move on to another location

Element 12. Sample Handling and Custody

The field coordinator will be responsible for ensuring that each field sampling team adheres to proper custody and documentation procedures. A master sample logbook of field data sheets shall be maintained for all samples collected during each sampling event. A chain-of-custody (COC, Attachment 1) form must be completed after sample collection, archive storage, and prior to sample release.

Grebe blood samples will be stored in glass or plastic vials on wet or dry ice in the field, then stored in the laboratory at -20C. Grebe eggs will be stored in polyethylene bags on wet ice in the field and then transferred to a refrigerator, until dissection within 6 months. After dissection, egg contents will be stored frozen in glass or plastic jars at -20C. Samples delivered to USGS-FRESC or USGS-WERC will be logged upon arrival.

Fish samples will be wrapped in aluminum foil and frozen on dry ice for transportation to the storage freezer or laboratory, where they will be stored at -20°C until dissection and homogenization. Samples delivered to MPSL-DFG will be logged in according to MPSL-104 (Appendix III C).

Sport fish samples will be dissected according to MPSL-105 (Appendix III D) and data retained on the lab data sheets in Attachment 4. Small fish samples will be processed according to the USGS Sample Preparation SOP (Appendix IV C).

Lab homogenates will be frozen until analysis is performed. Frozen tissue samples have a 12 month hold time from the date of collection. If a hold-time violation has occurred, data will be flagged appropriately in the final results.

Element 13. Analytical Methods

Methods and equipment for laboratory analyses are listed in Table 11. EPA methods can be downloaded from www.epa.gov/epahome/index/nameindx.htm. EPA method numbers followed by “M” indicate modifications have been made. Modifications and non-EPA SOPs can be found

in Appendix III and IV. Method validation data for modifications and SOPs can be obtained by contacting the analytical laboratory (Table 1.)

Table 11. Methods for laboratory analyses

Parameter	Method	Instrument
Mercury in Grebe Tissues	EPA 7473 (USEPA 1998)	Milestone DMA 80
Mercury in Fish Tissues	EPA 7473 (USEPA 1998)	Milestone DMA 80

An AWS brand AMW-DISC digital pocket scale, or similar, is used to weigh fish in the field and is calibrated monthly in the lab with standard weights. Fish lengths are determined using a fish measuring board that does not require calibration. No other field measurements are being taken.

Mercury in fish tissues will be analyzed according to EPA 7473, “Mercury in Solids and Solutions by Thermal Decomposition, Amalgamation, and Atomic Absorption Spectrophotometry” (USEPA, 1998) using a Direct Mercury Analyzer (DMA 80). Samples, blanks, and standards will be prepared using clean techniques. ASTM Type II water and analytical grade chemicals will be used for all standard preparations. A continuing calibration verification (CCV) will be performed after every 10 samples. Initial and continuing calibration verification values must be within $\pm 20\%$ of the true value, or the previous 10 samples must be reanalyzed. Three blanks, a certified reference material (DORM-3 or similar), as well as a method duplicate and a matrix spike pair will be run with each analytical batch of samples. Reporting Limits (RL) can be found in Table 12 and Measurement Quality Objectives (MQO) in Section 7, Table 9.

Table 12. Trace metal analytical parameters, reporting units, and reporting limits (RL) for tissue samples.

Parameter	Method	RL ($\mu\text{g/g}$ wet wt)
Mercury in Grebe Tissues	EPA 7473 (USEPA 1998)	0.004
Mercury in Fish Tissues	EPA 7473 (USEPA 1998)	0.009

13.2.1. Corrective Action

It is the responsibility of each analyst to take corrective action upon instrument failure. Corrective action will be conducted according to manufacturer or method specifications. Additional information on corrective actions can be found in Section 20.2.

13.2.2. Turn around time

All tissue analyses must be completed within the 1 year hold time. In addition, results need to be reported according to the timeline outlined in Table 7.

13.3. Sample Disposal

The laboratories are responsible for complying with all Federal, State and local regulations governing waste management, particularly hazardous waste identification rules and land disposal restrictions. Chemicals must be appropriately neutralized prior to disposal or must be handled as hazardous waste.

Element 14. Quality Control

MPSL-DFG and DFG-WPCL conduct quality control through several activities and methods. These methods of quality control are performed to identify possible contamination problem(s), matrix interference and the ability to duplicate/repeat results. When control limits are exceeded the Laboratory QAO will review with appropriate laboratory staff to ascertain the possible cause of the exceedance. A review of SOPs will be conducted and any deficiencies will be identified, documented, and corrected. A written report of the corrective action(s) will be provided to the PI and PM via email. The PM will contact the SWAMP QAO as needed.

Each aspect of laboratory quality control is listed in Table 9 for frequency as well as Measurement Quality Objectives (MQO) for each.

Element 15. Instrument/Equipment Testing, Inspection and Maintenance

Laboratory instruments are inspected and maintained in accordance with lab SOPs, which include those specified by the manufacturer and those specified by the method (Table 13). These SOPs have been reviewed by each respective Laboratory QAO and found to be in compliance with SWAMP criteria. Analysts are responsible for equipment testing, inspection, and maintenance. Appendices III and IV list the referenced SOPs. USGS SOPs are available upon request from the Laboratory Director by email: ceagles-smith@usgs.gov. Likewise, MPSL-DFG SOPs are available upon request from the Laboratory QAO by email: bonnema@mlml.calstate.edu.

Electronic laboratory equipment usually has recommended maintenance prescribed by the manufacturer. These instructions will be followed as a minimum requirement. Due to the cost of some laboratory equipment, back up capability may not be possible. But all commonly replaced parts will have spares available for rapid maintenance of failed equipment. Such parts include but are not limited to: batteries; tubes; light bulbs; tubing of all kinds; replacement specific ion electrodes; electrical conduits; glassware; pumps; etc.

The lead chemist, or designee, is responsible for the testing, inspection, and maintenance of equipment. Each instrument has its own logbook where the results of tests, inspections, maintenance and repairs are documented. When an instrument's test results fail to meet

accuracy and/or precision criteria after the lead chemist has performed maintenance, the manufacturer will be contacted.

Element 16. Instrument/Equipment Calibration and Frequency

Laboratory instruments (listed in Table 13) are calibrated, standardized and maintained according to procedures detailed in laboratory SOPs (Appendix I). Instrument manuals identify step-by-step calibration and maintenance procedures. Instruments and types of calibration required are listed in Table 13. If analytical instrumentation fails to meet performance requirements, the instrument(s) will be checked according to their respective SOP(s) and recalibrated. If the instrument(s) does again does not meet specifications, it will be repaired and retested until performance criteria are achieved. The maintenance will be entered in the instrument log. If sample analytical information is in question due to instrument performance, the PM will be contacted regarding the proper course of action including reanalyzing the sample(s).

At a minimum all calibration procedures will meet the requirements specified in the US EPA approved methods of analysis. The means and frequency of calibration recommended by the manufacturer of the equipment or devices as well as any instruction given in an analytical method will be followed. When such information is not specified by the method, instrument calibration will be performed at least once daily and continuing calibration will be performed on a 10% basis thereafter except for analysis by GC/MS. It is also required that records of calibration be kept by the person performing the calibration and be accessible for verification during either a laboratory or field audit.

Table 13. Equipment maintenance and calibration frequency.

Instrument	Inspection/Maintenance Frequency	Calibration Frequency
Milestone DMA-80 Direct Mercury Analyzer (USGS)	As needed	At least once every 2 weeks
Milestone DMA-80 Direct Mercury Analyzer (MPSL-DFG)	As needed	At least once every 2 weeks

16.1. Analytical Instrumentation

16.1.1. Instrument calibration

Upon initiation of an analytical run, after each major equipment disruption, and whenever on-going calibration checks do not meet recommended MQOs, the system will be calibrated with a full range of analytical standards. Immediately after this procedure, the initial calibration must be verified through the analysis of a standard obtained from a different source than the standards used to calibrate the instrumentation, prepared in an independent manner, and ideally having certified concentrations of target analytes of a CRM or certified solution. Frequently, calibration standards are included as part of an analytical run, interspersed with actual samples. However, this practice does not document the stability of the calibration and is incapable of detecting

degradation of individual components, particularly pesticides, in standard solutions used to calibrate the instrument. The calibration curve is acceptable if it has an R^2 of 0.990 or greater for all analytes present in the calibration mixtures. If not, the calibration standards, as well as all the samples in the batch are re-analyzed. All calibration standards will be traceable to a recognized organization for the preparation and certification of QC materials (e.g., National Institute of Standards and Technology, National Research Council Canada, US EPA, etc.).

Calibration curves will be established for each analyte and batch analysis from a calibration blank and a minimum of three analytical standards of increasing concentration, covering the range of expected sample concentrations. Only data which result from quantification within the demonstrated working calibration range may be reported (i.e., quantification based on extrapolation is not acceptable). Alternatively, if the instrumentation is linear over the concentration ranges to be measured in the samples, the use of a calibration blank and one single standard that is higher in concentration than the samples may be appropriate. Samples outside the calibration range will be diluted or concentrated, as appropriate, and reanalyzed.

16.1.2. Continuing calibration verification (CCV)

Calibration verification solutions traceable to a recognized organization are inserted as part of the sample stream. The sources of the calibration verification solutions are independent from the standards used for the calibration. Calibration verification solutions used for the CCV will contain all the analytes of interest. The frequency of these verifications is dependent on the type of instrumentation used and, therefore, requires considerable professional judgment. The required frequency for this project is listed in Table 9. All analyses are bracketed by an acceptable calibration verification; all samples not bracketed by an in control CCV should be reanalyzed. If the control limits for analysis of the calibration verification solution are not met, the initial calibration will have to be repeated. All samples analyzed before the calibration verification solution that failed the MQOs will be reanalyzed following the recalibration. Only the re-analysis results will be reported. If it is not possible or feasible to perform reanalysis of samples, all earlier data (i.e., since the last successful calibration control verification) are suspect. In this case, the laboratory QAO will contact the PM to determine proceedings, and will flag the data and note the issue in interim and final reports.

Element 17. Inspection/Acceptance of Supplies and Consumables

All supplies will be examined for damage as they are received. Laboratory ordering personnel will review all supplies as they arrive to ensure the shipment is complete and intact. All chemicals are logged in to the appropriate logbook and dated upon receipt. All supplies are stored appropriately and are discarded upon expiration date. Table 14 indicates items that are considered for accuracy, precision, and contamination. If these items are not found to be in compliance with the acceptance criteria, they will be returned to the manufacturer.

Table 14. Inspection/acceptance testing requirements for consumables and supplies.

Project-Related Supplies (source)	Inspection / Testing Specifications	Acceptance Criteria	Frequency	Responsible Individual
Certified pre-cleaned glass or plastic (I-Chem/Fisher Scientific or similar)	Carton custody seal is inspected	Carton custody seal intact	At receipt date of shipment	USGS or MSPL-DFG personnel
Nitrile Gloves (Fisher Scientific or similar)	Carton seal is visually inspected for damage or tampering	Carton is intact and gloves within are clean and intact	At receipt date of shipment	USGS or MSPL-DFG personnel
Polyethylene Gloves (Fisher Scientific or similar)	Carton seal is visually inspected for damage or tampering	Carton is intact and gloves within are clean and intact	At receipt date of shipment	USGS or MSPL-DFG personnel
Analytical Standards (Perkin-Elmer, VWR, Fisher Scientific or similar)	Solution bottles are inspected to verify factory seal	Manufacturer's seal intact	At receipt date of shipment	USGS or MSPL-DFG personnel

Element 18. Non-Direct Measures

Data will not be used from non-direct measures in this study.

Element 19. Data Management

Field data will be entered into the SWAMP Database version 2.5 upon return to the lab. Original field sheets (Attachment 1) will be retained in a log book, and copies of the COCs (Attachment 2) will be kept by each receiving laboratory. SWAMP Authorization forms will also accompany samples sent to each laboratory (Attachment 3).

All data generated by USGS will be maintained as described in USGS SOPs (Appendix IV) and the USGS QAP (Appendix I). The USGS QAO will be responsible for oversight of the collection of all organic chemical analysis data and entering QA-checked data into the SWAMP database.

Likewise, all MPSL-DFG data will be generated and maintained according to the Marine Pollution Studies Laboratory Quality Assurance Plan (Appendix I). The MPSL-DFG QAO will be responsible for oversight of the collection of all dissection and metals analysis data and entering QA-checked data into the SWAMP database.

All data collected will be entered into electronic spreadsheets that are SWAMP compatible. Each data element is checked at a minimum by the technician that entered the data and verified by the technician's signature on the data sheet. Tissue data will be provided to the PC in Microsoft Excel spreadsheets. Data will be reviewed to ensure they are consistent with the format of the database and other data records.

All raw and statistical analysis data are subject to a 100% check for accuracy by the PM and Laboratory QAOs. Data are analyzed and proofread for accuracy, and then QA checked against

the QAPP and SWAMP criteria before being entered into the SWAMP database. Original hard copies of the data are filed in a secure cabinet until requested by the PM and/or inclusion into the Final Report. Electronic copies are stored and backed up by each analyst and respective laboratory internal project manager.

Hardware and software will be updated as recommended by the manufacturer or as needed. Testing of each component is not required on a regular basis aside from day to day functionality. Each entity is responsible for the necessary updates or upgrades, whether provided regularly through an Information Technology department or otherwise.

Data management checklists are not required. Analytical completeness will be tracked through the SWAMP Database version 2.5.

Group C Elements: Assessment and Oversight

Element 20. Assessments and Response Actions

20.1. Audits

All reviews of QA data will be made by the QAO of each laboratory prior to submission of each batch to the USGS or SWAMP Tissue Database 2.5. Reviews of the sampling procedures will be made by the Field Collection Coordinator and the Project Coordinator in case problems occur. As SOPs are updated and refined, additional reviews will be made. Each data technician is responsible for flagging all data that does not meet established QA/QC criteria.

Project data review established for this project will be conducted once all data sets have been received, and includes the following:

- Initial review of analytical and field data for complete and accurate documentation, chain of custody procedures, compliance with analytical holding times, and required frequency of laboratory QA samples.
- Comparison of all spike and duplicate results with the MQOs in Table 9.
- Assigning data qualifier flags to the data as necessary to reflect limitations identified by the process.

If a review discovers any discrepancy, the QAO will discuss it with the personnel responsible for the activity. The discussion will include the accuracy of the information, potential cause(s) leading to the deviation, how the deviation might impact data quality and the corrective actions that might be considered. If the discrepancy is not resolved, the QAO will issue a stop work order until the problem is fixed.

Assessments by the QAO will be oral; if no discrepancies are noted and corrective action is not required, additional records are not required. If discrepancies are observed, the details of the discrepancy and any corrective action will be reported and appended to the report.

All assessments will be conducted as data is received by the laboratory QAO in accordance with the timeline in Table 7.

20.2. Deviations and corrective actions

Analyses are conducted according to procedures and conditions recommended by the US EPA and described in laboratory SOPs (Appendices III and IV), with the exception of those reported herein. Beyond those identified, deviations from these recommended conditions are reported to the Laboratory QAO. The PM will be notified within 24 hours of these deviations.

In the event of a SOP/QAPP deviation or corrective action, a deviation/corrective action form will be prepared, completed, signed and the PM notified. Best professional judgment will be used in interpretation of results obtained when deviations in the test conditions have occurred. All deviations and associated interpretations will be reported in interim and final reports. Protocol amendments will be submitted to the Laboratory QAO and PM. Upon approval, protocol amendments will be employed.

This study strives for 90% analytical data completeness. If this goal cannot be achieved, various corrective actions can be undertaken as described in Section D24.

Element 21. Reports to Management

The following products are to be delivered to PM:

- Each LD shall regularly brief the PC, LS and PM on the progress of all on-going chemical analyses in monthly emails or conference calls. When deemed necessary for decision making, other BOG participants will also be notified of progress.
- The LS will provide a draft final report and a final report to the PM in accordance with the dates listed in Table 7.

Group D Elements: Data Validation and Usability

Element 22. Data Review, Verification and Validation Requirements

All data reported for this project will be subject to a 100% check for errors in transcription, calculation and computer input by the laboratory internal project manager and/or laboratory QAO. Additionally, the Laboratory QAO will review sample logs and data forms to ensure that requirements for sample preservation, sample integrity, data quality assessments and equipment calibration have been met. At the discretion of the LD, data that do not meet these requirements will either not be reported, or will be reported with qualifiers which serve as an explanation of any necessary considerations.

Reconciliation and correction will be decided upon by the Laboratory QAO and LD. The Laboratory QAO will be responsible for informing data users of the problematic issues that were discussed, along with the associated reconciliations and corrections.

Data generated by project activities will be reviewed against the measurement quality objectives (MQOs) in Table 9. Furthermore, the final dataset as a whole will be scrutinized for usability to answer the three Management Questions.

Element 23. Verification and Validation Methods

Grebe tissue data will be reported electronically to the USGS database managers. The data will be validated according to USGS procedures.

Fish data will be reported electronically to the Project Coordinator, then to the SWAMP Database Management Team (DMT) for inclusion in the SWAMP Database version 2.5. The DMT will follow SWAMP SOP Chemistry Data Verification V1.1 (Appendix V A).

All data will be validated by according to BOG Data Validation (Appendix V B), outlined below. Please refer to the appended document for complete descriptions and validation steps, as well as examples of potential QC failures.

QA narratives will be produced to be incorporated in the BOG Wildlife Report. This narrative will summarize the data set from a QA standpoint. Validated data will be made available to users via the State Water Resources Control Board CEDEN website (<http://www.ceden.us/AdvancedQueryTool>).

23.1. Blank Contamination Check

Blank verification samples identify if the target analyte has contaminated field samples via lab contamination from any part of sample preparation and analysis. One method blank (laboratory derived) sample is run with each analytical batch (≤ 20 samples). The method blanks will be processed through the entire analytical procedure in a manner identical to the field samples. The ideal scenario is that method blank samples are non-detects. If a field sample is contaminated from laboratory procedures and the analytical quantification of that field sample is low, then a high proportion of the field sample value could be from laboratory contamination which results in that value being uncertain and not usable. Laboratory blank contamination could result in a false positive when field sample results are low. There is less concern of blank contamination affecting a field sample if field samples are some multiple higher than the method blank result (in this case 3 times the method blank concentration).

Please refer to BOG Data Validation Standard Operating Procedure (Appendix V B) for details on the steps taken to determine blank contamination.

23.2. Accuracy Check

Accuracy is the degree of agreement of a measurement with a known value and is utilized to assess the degree of closeness of field samples to their real value. Using the bull's-eye analogy, accuracy is the degree of closeness to the bull's-eye (which represents the true value). Over/under estimation of analytical quantification is important in this project. If the QA elements indicate overestimation of the field sample result than this could lead to false positives above particular human health consumption thresholds and potentially limit human consumption of particular sport fish species. If the QA elements indicate underestimated analytical quantification then low field sample values could falsely suggest that fish are below human health thresholds when they may actually be above the thresholds. Good accuracy in a data set increases the confidence and certainty that the field sample value is close to the true value. Accuracy is determined by such QC elements as: certified reference materials (CRM), laboratory control samples, blind spikes, matrix spikes, and performance samples.

Please refer to BOG Data Validation Standard Operating Procedure (Appendix V B) for details on the steps taken to determine accuracy.

23.3. Precision Check

Precision is the degree to which repeated measurements under unchanged conditions show the same result (usually reported as a relative standard deviation [RSD] or relative percent difference [RPD]). The repeatability measure indicates the variability observed within a laboratory, over a short time, using a single operator, item of equipment, etc. These QA elements also show the reproducibility of an analytical measurement. Good precision provides confidence that the analytical process is consistently measuring the target analyte in a particular matrix.

Please refer to BOG Data Validation Standard Operating Procedure (Appendix V B) for details on the steps taken to determine precision.

Element 24. Reconciliation with User Requirements

Data will be reported in the SWAMP Database version 2.5. Data that do not meet with the Measurement Quality Objectives in Table 9 will be flagged accordingly as discussed in Section D23. Rejected data will not be included in data analyses while data flagged as estimated will be evaluated for inclusion on a case-by-case basis in conjunction with the associated QA data and program objectives.

The project needs sufficient data, as represented by the completeness objective (Table 8), to address the management questions laid out in the Sampling Plan (Appendix II). A failure to achieve the number of data points cited could mean an inability to answer these questions.

To address MQ1, concentrations of mercury in avian tissues will be compared to effect thresholds from the literature and concentrations in small fish will be compared to the threshold for small fish to be established by the State Water Board.

To address MQ2, we will use mixed-effects general linear model to test whether lake-specific mean THg concentrations in avian tissues can be determined using lake-specific mean THg concentrations in small fish sampled during a similar timeframe. We will compare the strength of models that incorporate a suite of factors, including region, elevation, and lake size to determine if there are category specific factors that can be used to refine biomagnification factor estimates.

To address MQ3, successful elements of the sampling and analysis plan will be recommended as valuable components of TMDL-related monitoring.

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