Development of Sediment Quality Objectives for California Bays and Estuaries

Work Plan for:
Using Biota-Sediment Accumulation Models to Develop Sediment Chemistry Indicators

Revised October 18, 2004

Background

The State Water Resources Control Board of California (SWRCB) has been mandated to develop sediment quality objectives (SQOs) that protect beneficial uses of California's bays and estuaries. Substantial effort is underway to identify sediment contaminant thresholds, based on direct effects to organisms residing in the sediments. However certain chemicals of concern are subject to biomagnification, a process that results in elevated concentrations in higher trophic levels of the food web through feeding interactions and the dietary uptake of chemicals. In these situations sediment contamination can also affect other organisms in the benthic and the benthic-pelagic food webs as well as species that ingest these organisms such as birds, marine mammals and terrestrial mammals including humans.

Many wildlife species, including bald eagles, nesting birds, and turtles, are primarily dependent on aquatic organisms such as fish and crustaceans for food. Numerous studies have demonstrated that sediment-associated hydrophobic compounds, such as DDT, polychlorinated biphenyls (PCBs), and methyl mercury, bioaccumulate and cause deleterious effects at relatively low concentrations (see for example, Beyer et al. 1996). California provides critical habitat for 154 endangered and threatened species (California Code of Regulations, Title 14, Section 670.5). As such, it is important that the SQOs developed for California consider the impact of sediment quality on the health and well-being of endangered species and wildlife.

Contaminant bioaccumulation[1] is an important but challenging issue in evaluating sediment quality. The health of sensitive local fish and piscivorous wildlife can be adversely impacted as a result of contaminant bioaccumulation through indirect interactions with the sediment. Contaminants in fish can also reach concentrations sufficient to pose potential health risks to sport and subsistence anglers. Given these potential risks, the State of California water quality policy stipulates that SQO development should address human health[2]. Nevertheless, the relationships between contaminant concentrations in sediments and biota are complex and variable. The

[1] Bioaccumulation is a process in which the chemical concentration in an organism achieves a level that exceeds that in its surrounding environment (i.e. water) as a result of chemical uptake through all routes of chemical exposure (e.g. dietary and dermal absorption and transport across the respiratory surface).
[2] California Water Code 13393.b. "The state board shall base the sediment quality objectives on a health risk assessment if there is a potential for exposure of humans to pollutants through the food chain to edible fish, shellfish, or wildlife."

development of SQOs to protect wildlife, fish, and human health will incorporate a multiple line of evidence approach, similar to that under development for direct effects on aquatic life (see multiple line of evidence workplan). One of the lines of evidence to be used will be a sediment chemistry. The project described in this work plan will refine methods for developing bioaccumulation-based sediment chemistry indicators to protect wildlife and human health in California bays and estuaries.

The development of chemistry indicators based on bioaccumulation requires two components: 1) an effects threshold for the target organism and; 2) a robust relationship between contaminant concentrations in sediments and the target organism. The ratio between concentrations in the target organism (C_B) versus sediment concentrations (C_S) is defined as the biota-sediment accumulation factor (i.e., BSAF = C_B/C_S). A number of difficulties arise when attempting to predict BSAFs. At a given site, a portion of an organism's contaminant body burden may result from uptake from other sources, such as the overlying water column. Although specific case studies indicate that certain contaminants are accumulated from the sediments (e.g., Connolly 1991; Gobas and Wilcockson 2002), this could vary on a site by site basis. For vagile organisms, variation in home range can affect the relative impact of contamination at a specific site as a result of the heterogeneous distribution of chemicals in the sediment. This spatial variation can be addressed using spatially explicit models that partition fish exposure based on migratory patterns (Linkov et al. 2002). Variations in food web structure among locations can also cause differences in contaminant bioaccumulation (Gobas and Wilcockson 2002). On a regional scale, variability among sites in BSAFs can occur due to differences in animal species sampled, trophic position, sediment properties, and tissue lipid concentration. These factors can all be critically evaluated using currently available empirical and mechanistic models (reviewed in U. S. EPA 2000).

Bioaccumulation models typically involve a combination of empirical and mechanistic models. In the empirical modeling approach, BSAFs are deduced from measured concentrations in organisms and sediments, as well as ancillary variables known to be influential. Mechanistic models use equations to quantify the specific contaminant uptake and loss processes (e.g., respiration, feeding, absorption, and excretion), in order to predict concentrations in biota of a specific ecosystem (Mackay and Fraser 2000). Empirical models have fewer data requirements than mechanistic models, and are easier to calculate; they can be readily used to develop statistical associations between biota and sediment contamination (Mackay and Fraser 2000; U. S. EPA 2000). Therefore, empirical models are readily applied to derive sediment chemistry indicator values for large regional datasets. However, the predictive capacity of empirical models is limited, resulting in the recommendation that they be used only as screening assessment tools to identify high risk sediments requiring further evaluation (Wong et al. 2001). Because mechanistic models must be parameterized using local data on food web transfer pathways and biota uptake and loss processes, they are not typically applied at broad regional scales (Arnot and Gobas 2003 provide an exception). Mechanistic models can be used to better understand the drivers of BSAF at a particular location, by corroborating empirical field data and quantifying the impact of other factors such as water contamination.

Current government-established sediment quality guidelines generally don't address contaminant bioaccumulation and consequent toxicity to higher trophic levels. Nevertheless, human health and wildlife risk assessment is frequently undertaken to establish guidelines at specific water bodies. Sediment quality guidelines developed by Florida and Canada focus on effects to benthic invertebrates, and do not include indirect effects due to bioaccumulation (MacDonald 1994; Canadian Council of Ministers of the Environment 1999). In Washington, statewide sediment quality guidelines are established based on compilation of toxicity data from freshwater benthic organism bioassays (SAIC and Avocet Consulting 2002; Michelsen 2003), but local case studies do use empirical finfish BSAFs to establish human health based criteria (Weiss 1997). Guidelines developed in New York do address potential hazards posed to wildlife and human health, but contaminant bioavailability is estimated as a function of equilibrium partitioning into pore water, rather than direct measurement or estimation of food web trophic transfer (New York State Department of Environmental Conservation 1999). Despite the absence of bioaccumulation-based statewide criteria, many studies have documented significant relationships between contaminant concentrations in sediments and associated fish (Endicott and Cook 1994; Wong et al. 2001; Zeng and Tran 2002; Burkhard et al. In press). The purpose of this project is to develop recommended sediment quality objectives for California waters based on trophic transfer of contaminants and consequent toxicity to fish, wildlife, and humans. Given the potential for uncertainty in the results, this project will also clearly document the methodology and assumptions used to develop bioaccumulation-based sediment quality objectives, and provide detailed case study examples, for local sediment quality objective development.

Of the target contaminants for indicator development, trace metals are particularly difficult to calculate predictive BSAFs. Some scientists argue that metals require the collection of site-specific data for valid assessment of bioaccumulation from sediment (reviewed in Lee and Jones-Lee 2003). Even bioavailability of metals to benthic detritivores is complex, influenced by the concentration of metals compared to abundance of binding molecules (Hansen et al. 1996), requiring ancillary data frequently not collected in monitoring programs. In contrast, nonpolar organic compounds exhibit bioaccumulation patterns that are reasonably predicted by a chemical's octanol-water partition coefficient (K_{ow}), sediment organic carbon, and biota whole body lipid content (Clark et al. 1988; Thomann 1989; U. S. EPA 2000). Given these factors and the need to set priorities in a limited time frame, this study will focus on nonpolar organics, including polychlorinated biphenyls (PCBs), DDTs, chlordane, toxaphene, dibenzodioxins, dibenzofurans, and polybrominated diphenyl ethers (PBDEs).

Objectives

This work plan focuses on evaluating biota-based sediment chemistry indicator values, by comparing California datasets to empirical and mechanistic contaminant bioaccumulation models (Mackay and Fraser 2000; U. S. EPA 2000; Burkhard et al. 2003b).

This project has six scientific objectives:

1. Estimate sediment concentrations that would be protective of selected California bays and estuaries, based on effects thresholds for humans and wildlife consuming fish and benthic organisms.
2. Identify bioaccumulation models that predict relationships between biota and sediment contaminant concentrations for bays and estuaries of California.
3. Identify taxonomic and regional groupings that appear to result in stronger statistical correlations between biota and sediment contaminant concentrations across regional scales.
4. Determine statistical strength and uncertainty of empirical relationships between biota and sediment contaminant concentrations.
5. Demonstrate a mechanistic bioaccumulation model for a range of hydrophobic organic contaminants in two separate local case studies.
6. Evaluate the potential impact of factors, such as contamination in water, variation in fish home range size, and diet, on modeled sediment chemistry values.

General Approach

These objectives will be addressed in two tasks. In Task 1, several types of empirical models will be assessed using a broad scale examination of contaminant transfer from sediment to biota. The empirical modeling task will address objectives 1-4, listed above. The relationships between contamination in biota (bivalves and fish) and sediments will be investigated using available data. This task will identify cases where specific criteria may be applied on a regional or statewide basis.

A mechanistic food web bioaccumulation model will be compared to empirical model results to develop bioaccumulation-based sediment chemistry thresholds for two local case studies in Task 2. The local case studies will address project objectives 1, 5, and 6 listed above, including development of sediment quality thresholds for certain organic contaminants. For this exercise, thresholds will be back calculated based on health risks to fish, in addition to human and piscivorous wildlife. The results of the mechanistic model will also be compared to empirical modeling results, in order to determine degree of confidence in local bioaccumulation estimates.

Work Description

Task 1: Evaluate Empirical Partitioning Models for Statewide Application. If bioaccumulation is to be one of the bases for establishing SQOs, significant relationships should be quantified between contaminant concentrations in biota and concentrations in sediments using simple bioaccumulation models. Additionally, appropriate effects thresholds for target species (i.e., fish and shellfish, as well as human and wildlife piscivores) must be identified. The target effects thresholds in biota could then be combined with the empirical relationship between biota and sediment concentrations to establish sediment chemistry values for use in a multiple line of evidence evaluation.

A number of empirical approaches are available for estimating the relationship between biota and sediment contaminant concentrations. These are generally considered to be predictive for hydrophobic organic contaminants, including DDTs, dieldrin, PCBs, chlordanes, toxaphene, and dioxins. The statewide evaluation of empirical data will focus on two modeling approaches: normalized biota-sediment accumulation factors (BSAFs), and uncorrected bioaccumulation factors (BAF).

Normalized Biota-Sediment Accumulation Factors (BSAF). The normalized BSAF is the ratio of biota to sediment contamination concentration, corrected for lipid content of the biota and organic carbon content of the sediment (reviewed in Wong et al. 2001; Burkhard et al. In press). The ratio is defined by the following equation: BSAF = $(C_l/f_l)/(C_s/f_{oc})$, whereby C_l is a compound's concentration in tissue (preferably whole body tissue), f_l is the fraction of lipid in tissue, C_s is a compound's concentration in sediment, and f_{oc} is the fraction of organic carbon in sediment (U. S. EPA 2000 and references cited therein). The use of lipid and organic carbon normalization rests on the principle that many contaminants are predominantly associated with these matrices, causing there to be more reliable relationships when correcting for them (Clark et al. 1988). Organic carbon normalization has been supported by empirical evaluations of contaminant fractionation among sediment types in multiple datasets (Di Toro and De Rosa 1998).

BSAFs are typically derived on a site- and species-specific basis, using empirical data (e.g., Froese et al. 1998; Wong et al. 2001; Burkhard et al. In press). They incorporate the effects of metabolism, biomagnification, growth, and bioavailability. Accurate information on organism lipid content and sediment total organic carbon (TOC) content is needed for deriving a BSAF. BSAFs are most useful for systems that are in steady state (thermodynamic equilibrium), which is defined as a condition where chemical concentrations in sediment, water, and organisms do not change as a function of time, especially during the study period (U. S. EPA 2000 and references cited therein).

Uncorrected Bioaccumulation Factors (BAFs). A Bioaccumulation Factor (BAF) is the ratio of a chemical compund's concentration in tissue (C_t in mg/kg dry wt) to a compound's concentration in water (C_w in mg/L) or in sediment (C_s in mg/kg dry wt); i.e., for sediments, BAF = C_t/C_s. BAFs have the advantage of requiring no ancillary data other than biota and sediment contaminant concentrations. Given that these ancillary data are often unavailable, a larger dataset is available for estimating BAFs, than for normalized BSAFs. However, uncorrected BAFs may exhibit weak relationships due to variability in sediment properties and biota lipid concentrations. Empirically measured BAFs integrate all environmental routes of exposure and take into account the bioavailability of the chemical in the system being studied. Field-measured BAFs are especially important for compounds that have a log $K_{ow} > 6$, since prediction of bioaccumulation of these compounds is overestimated when based on their hydrophobicity alone. (U. S. EPA 2000 and references cited therein).

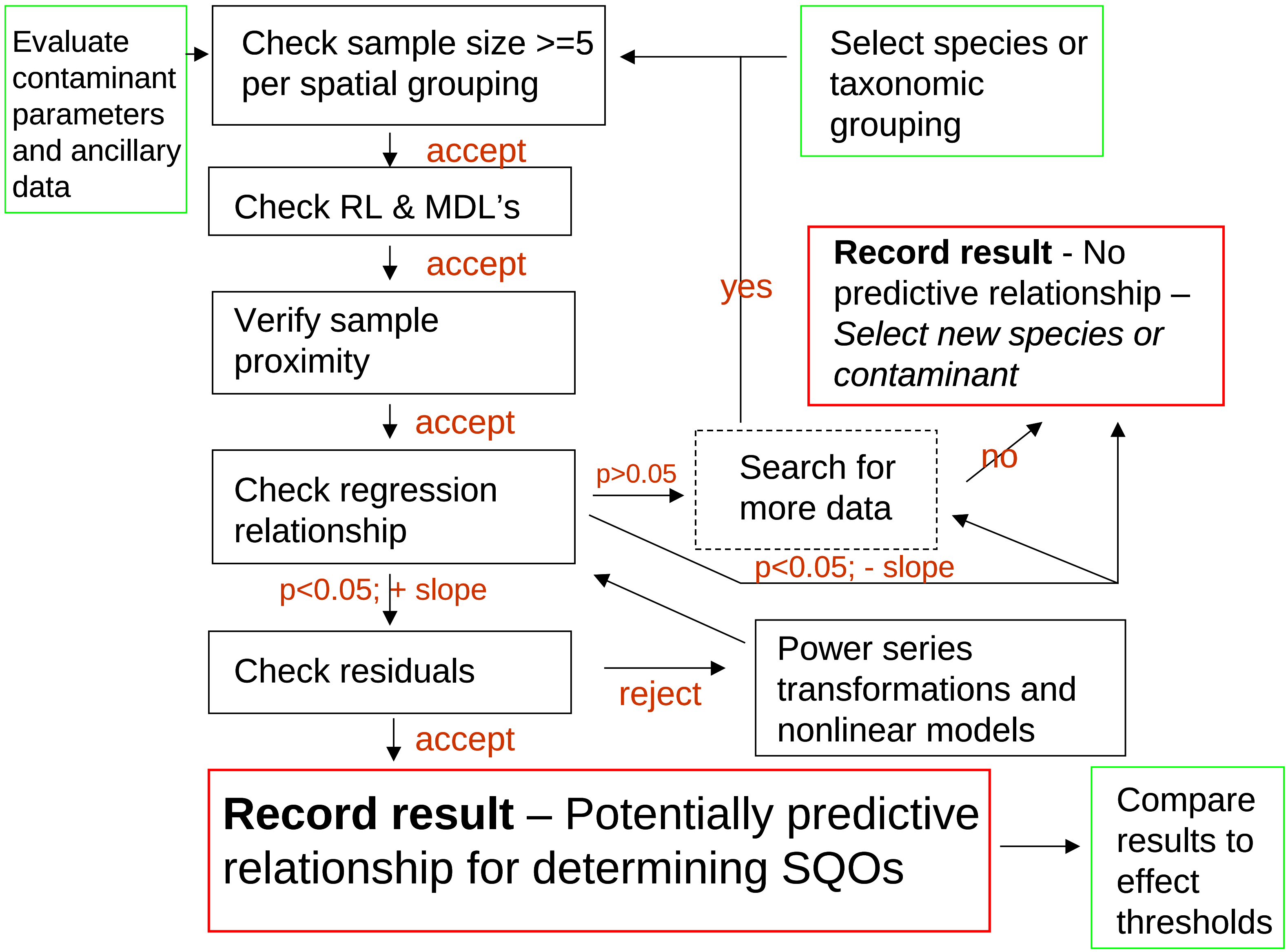
The models discussed above vary in input data requirements and predictive ability. Both assume that there is a consistent relationship between biota contaminant concentrations and sediment contaminant concentrations, provided that there are corrections for ancillary data (Clark et al. 1988). When thermodynamic equilibrium is reached, the BSAF typically ranges from 1 to 2. Equilibrium conditions may occur for short-lived benthic invertebrates, but fish and wildlife often exhibit BSAFs above or below these values, reflecting disequilibrium. For fish, BSAF can vary as a result of food web trophic transfer, lack of equilibrium between the sediments and water column, variation in benthic-pelagic coupling, and metabolic breakdown of contaminants (Burkhard et al. 2003a; Burkhard et al. In press). Equilibrium conditions occur in some local studies (e.g., Froese et al. 1998), but BSAFs often differ from equilibrium, as a result of these factors (Morrison et al. 1996; Wong et al. 2001; Burkhard et al. In press).

Subtask 1.1. Develop Dataset for Empirical BSAF Modeling. The main data source for this project will be the extensive California sediment quality objective (CASQO) database being developed as part of the overall SQO program. The database development process includes an initial QA screening of datasets having colocated sediment and biota contaminant concentrations (see sediment quality database work plan). If necessary, additional data sources may also be added. Potential data sources are extensive, and include State Mussel Watch Program, the Toxic Substances Monitoring Program, NOAA National Benthic Surveillance Project, and Environmental Monitoring and Assessment Program, the Regional Monitoring Program for Trace Substances in San Francisco Bay, U.S. Army Corps of Engineers Dredged Material Management Office data, superfund site data (e.g., Alameda Naval Station and Hunter's Point), and Southern California Bight Regional Monitoring Survey Program (Noblet et al. 2002).

Available data sources will be screened for attributes important for evaluation of relationships between sediment and biota contaminant concentrations. These include spatial and temporal proximity of sediment and biota collection, animal species likely to be in close proximity to sediments (e.g., bivalves and benthic fish species, Wong et al. 2001), and availability of ancillary data to estimate biota lipid and sediment organic carbon concentrations. The database screening procedures will be similar to those used to prepare the CASQO analysis dataset. The sediment quality objective (SQO) database will be used to evaluate proximity of sediment vs. biota samples. Samples will be considered to be from the same spatial proximity at a study site by matching station locations (e.g. station identification number or latitude and longitude).

Statistical and graphical analyses will only be performed on data that fit a number of minimum criteria. The process tree illustrated in Figure 1 provides additional detail on the approach for including field data in empirical model development. First of all, within a given analysis, a sample size of n >= 5 separate fish or invertebrate composites will be required. Data assigned as below the Reporting Limits (RLs) or Method Detection Limits will not be included. Data will only be used when biota and sediment collection sites are same for invertebrates, or within 300m of each other for fish. Upon acceptance of the previous steps of the process tree, regressions of sediment contaminant concentration versus biota contaminant concentration will be performed, as described in Subtask 1.3.

Figure 1. Algorithm for development of empirical BSAFs using CA field data. Further details are provided in Subtasks 1.1 and 1.3



Subtask 1.2. Select appropriate effects thresholds for statewide assessment. The California Water Code indicates that water and sediment quality objectives must be protective of humans and wildlife, provided that there is evidence of trophic transfer between contaminants in the water or sediments and the humans or wildlife. Since trophic transfer of contaminants is known to occur in California ecosystems, effects thresholds in fish tissue concentrations associated with the sediments, in addition to humans and wildlife that consume those fishes, will be evaluated. Effects to selected endangered species will also be considered. These tissue concentrations will then be used to calculate sediment chemistry indicator values based on the BSAFs developed in this work plan.

Given the requirement to protect ecosystem functions as well as human health, separate effects thresholds must be identified to protect humans, piscivorous wildlife, and fishes. Effects thresholds for impacts of contaminants on target organisms will be tabulated using peer-reviewed literature and local studies. Specific fish and benthic invertebrate species will be selected based on having sufficient data to develop robust biota-sediment accumulation factors. Preliminary evaluation of the CASQO database indicates that appropriate target species for statewide assessment include California halibut, Pacific staghorn sculpin, and *Macoma* clams (Table 1). For each species, effects thresholds will be identified for effects to that organism, in addition to effects to wildlife or human piscivores, as appropriate (Table 1). Literature values, and calculated effects thresholds selection will be evaluated and interpreted by convening a committee of fish, wildlife, and human health protection agency personnel (further described in Section 2.2, below).

Threshold effect data sets exist for general categories of animals (e.g., fish, mammals, and birds). This summary of effects thresholds will include relevant endpoints in humans (e.g., Brodberg and Pollock 1999), as well as fish and piscivorous wildlife (e.g., Beyer et al. 1996; PRC Environmental Management 1997). The following general data bases will be reviewed to determine their applicability: the Toxicity Reference Values for birds and mammals in San Francisco Bay (PRC Environmental Management 1997); the Canadian Tissue Residue Guidelines for the Protection of Wildlife Consumers of Aquatic Biota prepared by the Canadian Council Ministry of the Environment (Canadian Council of Ministers of the Environment 1998); the US Army Corps of Engineers Environmental Residue-Effects Database (ERED); and New York State's Fish Flesh Criteria for Piscivorous Wildlife (New York State Department of Environmental Conservation 1999).

For each contaminant and animal target, there are a range of potentially appropriate effects thresholds, each having different degrees of certainty. Additionally, thresholds must be sufficiently protective of endangered species, for which species-specific data may be limited. To account for this range of certainty, and provide thresholds that will protect endangered species, this project will select two separate effects thresholds for each endpoint listed in Table 1. One threshold will be concentrations below which there is no evidence of adverse impacts to health. Sediments associated with animal tissues below this threshold will be confirmed to be unimpaired, without any expected potential risk of indirect impacts to biota. For fish and wildlife, this threshold will be selected to be protective not only of the target species, but also of other endangered species expected to occur in California waters. For humans, these effects thresholds will be concentrations above which 1 in 1 million people would be expected to have increased risk of health impairment, based on estimated consumption rates of the 90th percentile of sport fish consumers.

The other threshold will be concentrations above which adverse impacts to health would be expected in the target organism. This threshold will be a concentration above which there is little doubt of adverse effects. For wildlife, EC50 tissue concentrations, or other published effects thresholds will be used to estimate effects thresholds. For humans, these thresholds will be concentrations above which 1 in 10,000 people would be expected to have increased risk of health impairment, based on estimated consumption rates of the 50th percentile of sport fish consumers.

Table 1. Candidate species for exposure and effects evaluation as part of bioaccumulation SQO scope of work. **Study** = whether species would be considered in statewide empirical evaluation (Task 1) or site-specific case studies (Task 2). **Target** = what target organism would be evaluated for effects thresholds (in Subtasks 1.2 and 2.2). **Invertebrate** = threshold for effects in invertebrates; **Fish =** thresholds for effects in fish; **Wildlife** = thresholds for effects in piscivorous wildlife; **Human** = thresholds for effects in human consumers of target fish.

Species	**Study**	**Target**	**Reason for inclusion**
California halibut (*Paralichthys californicus*)	Statewide (Task 1)	Human; Fish	Abundant CASQO data; many effects studies
Pacific staghorn sculpin (*Leptocottus armatus*)	Statewide (Task 1)	Wildlife; Fish	Abundant CASQO data
White croaker (*Genyonemus lineatus*)	S.F. Estuary (Task 2)	Human; Fish	Abundant data; elevated contamination; popular subsistence fish; model parameters already developed
Shiner surfperch (*Cymatogaster aggregata*)	S.F. Estuary (Task 2)	Wildlife; Fish	Abundant data; elevated contamination; high site fidelity; model parameters already developed
Delta smelt (*Hypomesus transpacificus*)	S.F. Estuary (Task 2)	Wildlife; Fish	Federally threatened fish species.
Chinook salmon (*Oncorhynchus tshawytscha*)	S.F. Estuary (Task 2)	Fish	Federally endangered fish species (for winter run)
Spotted sand bass (*Paralabrax maculatofasciatus*)	Newport Bay (Task 2)	Human; Fish	Abundant data; elevated contamination; popular sport fish
Arrow goby (*Clevelandia ios*)	Newport Bay (Task 2)	Wildlife; Fish	Elevated contamination; site fidelity; important prey species for wading birds

California killifish (*Fundulus parvipinnis*)	Newport Bay (Task 2)	Wildlife; Fish	Elevated contamination; site fidelity; important prey species for clapper rail
Clam (*Macoma spp.*)	Statewide (Task 1)	Human; Wildlife; Invertebrate	Abundant CASQO data
California brown pelican (*Pelecanus occidentalis californicus*)	Newport Bay; S.F. Estuary	Wildlife	Federally endangered bird species
California clapper rail (*Rallus longirostris obsoletus*)	Newport Bay; S.F. Estuary	Wildlife	Federally endangered bird species
California least tern (*Sterna antillarum browni*)	Newport Bay; S.F. Estuary	Wildlife	Federally endangered bird species

Subtask 1.3. Evaluate BSAF and BAF models. Statistical and graphical analyses will determine whether regional consistency is observed using BSAF or BAF models. If there are consistent patterns across sites, this would facilitate the development of regional sediment chemistry values, by allowing for extrapolation to sites lacking measured field data. Graphical analyses will include bivariate plots of contaminant concentrations in biota versus concentrations in sediment taken across a wide range of sites, evaluating models corrected for lipid and organic carbon, in addition to uncorrected models. The relationship between contaminant K_{ow} and BSAF will also be plotted (e.g., Zeng and Tran 2002), although the predictive strength of this relationship may be limited (Burkhard et al. In press).

The statistical approach employed will be General Linear Modeling (SAS Institute 1990). General Linear Models are able to incorporate both continuous predictor variables (i.e., linear regression) and categorical predictor variables (i.e., analysis of covariance). A number of predictor variables will be evaluated for potential influence on contaminant concentrations in biota. Continuous predictor variables will include contaminant concentrations in sediment, tissue percent lipid, and sediment percent organic carbon. Additionally, if water column particulate matter percent organic carbon (%OC) data are available, the ratio of water column (%OC) to sediment (%OC) may be calculated. This ratio may be a correlate of sediment vs. water column chemical disequilibrum (L. Burkhard, *Pers. comm.*), which can significantly affect BSAF and BAF (Burkhard et al. 2003a). Categorical predictor variables will include taxonomic grouping and sampling location. Significant region-wide relationships between contamination in biota and in sediment could facilitate empirical development of tissue-based sediment chemistry indicator values. In the event that it is not possible to establish regional scale patterns in BSAFs, the emphasis of the empirical modeling exercise will switch to documenting bioaccumulation relationships on local scales. In this case, bioaccumulation based sediment chemistry indicators would need to be developed on a site-specific basis.

Details on the modeling algorithm are presented in Figure 1 (see also Subtask 1.1). Using SAS 9.1 software, linear regression models will applied, incorporating continuous and categorical variables as described above. If a predictive relationship is derived (i.e. $p<0.05$; positive slope), residuals will be analyzed for the statistical assumptions of normality, variance homoskedasticity, and curvature. A power series of transformations will be utilized if assumptions of residual normality or variance homoskedasticity are violated and subsequent regressions derived on the transformed data. Quadratic or cubic models will be attempted if residual curvature is indicated (Draper and Smith 1998). If a non-predictive (i.e., $p>0.05$) or negative relationship (i.e., negative slope) is derived, further appropriate datasets will be searched for inclusion. If no additional data are suitable, a non-predictive result will be noted for the contaminant and taxonomic or regional grouping. Significant regression results with an associated positive slope relationship will be considered potentially appropriate for development of sediment chemistry thresholds, by back-calculating from biota effects thresholds.

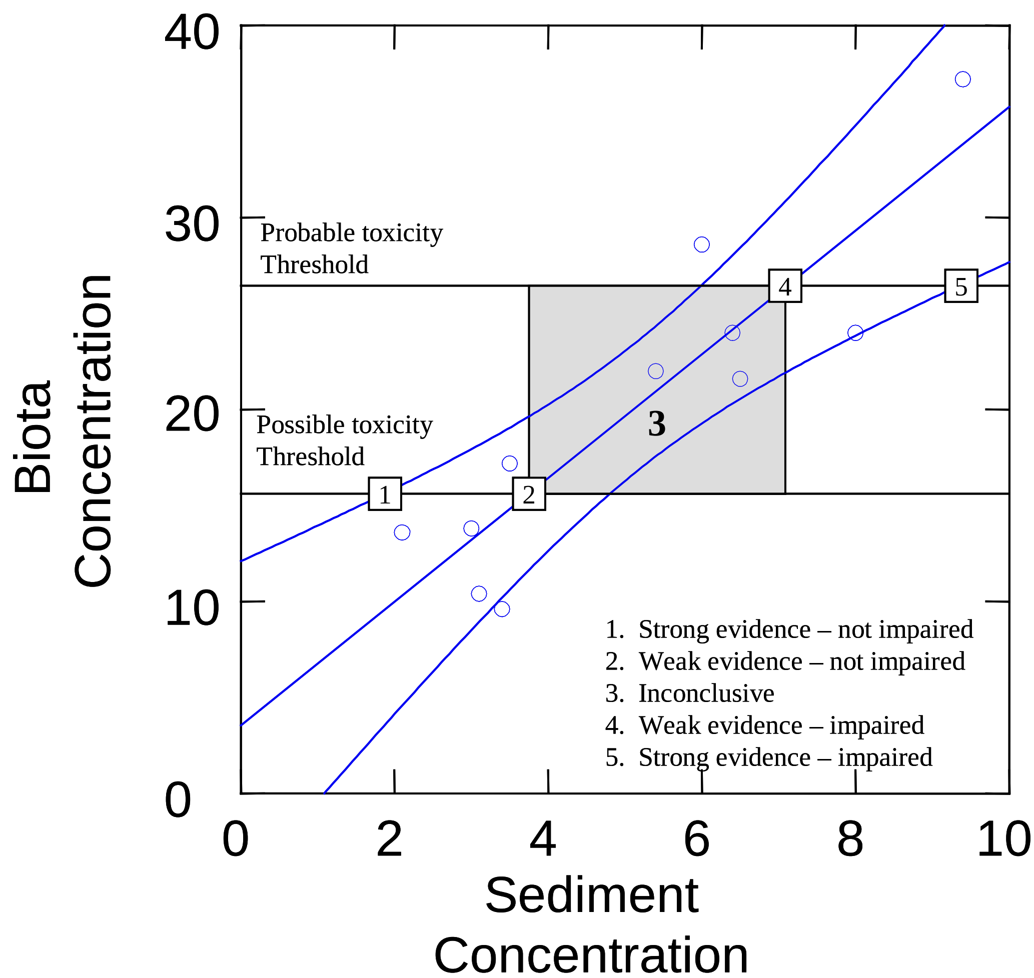
Regardless of whether regional or local models are ultimately used, acceptable models will be applied to develop a set of sediment chemistry threshold values. Figure 2 presents a general representation of the expected modeling approach. Following the experience developing thresholds in Washington State, more than one threshold is calculated, representing a range of exposure risks. In Figure 2, biota (i.e., fish or invertebrate) data are plotted vs. sediment data. Raw data from a site or group of sites are represented by circles, the best-fit regression line is represented by the straight diagonal line, and 95% confidence intervals around the mean regression line are presented by the two curved lines. Two toxicity thresholds for effects to the fish or their consumers (see Subtask 1.2), a “probable” and a “possible” toxicity threshold are represented by the two horizontal lines.

This statistical model of association between biota and sediment contamination and the two toxicity thresholds would be used to calculate four separate sediment chemistry thresholds, ranging in degree of impact represented. As seen in the figure, the intersection point between the best-fit regression and the two toxicity thresholds would represent sediment quality thresholds providing weak evidence of impairment vs. no impairment. That is, at sediment concentrations below “Point 2,” there would be weak evidence that sediment concentrations do not pose a toxicity risk to the target organism, and at sediment concentrations above “Point 4,” there would be weak evidence that sediment concentrations do pose a risk to the target organism. The intersection points between the 95% confidence interval of the mean regression line and the effects thresholds would provide strong evidence of impairment and no impairment. That is, sediment concentrations below “Point 1” do not pose a risk of toxicity to the target organism, and concentrations above “Point 5” would pose a risk. The gray area demarked “3” represents sediment contaminant concentrations at which no conclusion can be rendered regarding expected toxicity.

The use of multiple endpoints and uncertainty ranges account for potential limitations of the empirical data, and uncertainty regarding effects thresholds. The actual sediment quality objectives would be developed using a multiple line of evidence approach that incorporates these bioaccumulation-based sediment chemistry values, combined with other lines of evidence (e.g., tissue chemistry). The exact statistical modeling approach will be refined based on recommendations of consulting statisticians and modelers.

Subtask 1.4. Prepare report. These model comparisons and the methods used to conduct them will provide the basis for a technical report. The technical report will describe available models and methods for local sediment chemistry value determination based on empirical data and local effects criteria, and recommend appropriate methods given data availability and other local constraints. The technical report will provide guidance on appropriate methodologies for developing BSAFs using available California data. This document will be made available to the Scientific Steering Committee and other project participants for peer review. The revised technical report will also be included in the final Project Report.

Figure 2. Conceptual representation of statistical approach to be used in statewide empirical modeling efforts. See text for details.



Task 2: Apply a Mechanistic Bioaccumulation Model in Two Local Case Studies. A mechanistic food web bioaccumulation model will be applied to assess human and wildlife exposure due to fish consumption in two separate locations. The modeling

exercise will use a steady state non-equilibrium model developed to assess uptake of non-polar organic contaminants in food webs (Gobas 1993). This model simulates organic contaminant transfer from sediments and water through a multi-species food web by combining contaminant kinetics in biota (e.g., uptake and elimination) and food web dynamics (Gobas 1993; U. S. EPA 2000). The model has recently been updated to incorporate new research regarding phytoplankton uptake and elimination, fish and invertebrate ventilation rates, chemical partitioning and mechanisms of gastrointestinal magnification of contaminants (Morrison et al. 1996; Arnot and Gobas 2004). The mechanistic model has the advantage of quantifying the relative inputs of a particular chemical into an organism from the water versus from the diet. The latter measurement will be utilized in conjunction with food web interactions to estimate the direct contributions of sediment contamination to organisms throughout the food web.

This model has been selected because it is expected to incorporate adequate mechanistic detail, while being relatively easy to use and interpret. It has already been parameterized for local conditions as part of the PCB TMDL (Total Maximum Daily Loading) in San Francisco Bay (Gobas and Wilcockson 2002; Gobas and Arnot 2004), including a detailed food web study to parameterize and validate the model for PCB uptake (Roberts et al. 2002; Sigala et al. 2002). Parameterization for other contaminants in San Francisco Bay should be relatively straightforward, based on literature values for contaminant properties (Mackay et al. 2000) and locally available data on contaminant concentrations (SFEI 2002; Greenfield et al. 2004). It should also be possible to parameterize the model for use in other locations such as Newport Bay, as it requires a relatively small number of input parameters regarding organism physiology (e.g., wet weight, whole body lipid content and feeding preferences). In its present form, the model does not address temporal variability. More complex kinetic models would be required to incorporate time or age-dependant changes in biota concentrations or BSAFs (e.g., Borgmann and Whittle 1992).

The selected model will be applied to San Francisco Bay and Newport Bay. Both locations have extensive field data for parameter development and model validation. In each case study, mechanistic model findings will be corroborated by comparing the results to available empirical data. This will include comparing mechanistic modeling results on contaminant partitioning to actual observed partitioning between sediments and biota and the ecosystem. Where possible, empirical observed concentrations in sediments, benthic invertebrates, fishes, and wildlife will be compared to mechanistic model results. If the findings are consistent between the mechanistic models and empirical data, this will support the sediment chemistry thresholds developed. If the findings are not consistent, this will indicate that a combination of additional data collection and model calibration may be required.

The model will be used to estimate sediment concentrations that would result in human health guideline exceedances for locally consumed fish species. The model will also be used to estimate tissue concentrations that would result in adverse effects to fish and to endangered piscivorous birds, as a result of forage fish consumption (Table 1). A number of hydrophobic organic contaminants will be evaluated, varying based on management priorities and data availability for each location. Model estimated concentrations in biota will be compared to guidelines developed by the California Office of Environmental Health Hazard Assessment (e.g., Brodberg and Pollock 1999), locally derived thresholds for impacts to piscivorous wildlife (e.g., PRC Environmental Management 1997) or other locally developed exposure guidelines.

<u>Subtask 2.1. Parameterize model for case studies.</u> Parameter estimation is an important part of any modeling exercise, with parameter values chosen using literature and local data. For each case study, local data will be compiled and used to generate distributions and ranges model parameters. Local data will be particularly useful in estimating sediment contaminant concentration, water contaminant concentration, and food web structure. Based on previous sensitivity analyses in San Francisco Bay and other ecosystems, the model is likely to be relatively sensitive to particular environmental, biological and chemical parameters (Gobas and Arnot 2004). Influential environmental parameters will likely include contaminant concentrations in water and sediments, organic carbon content in water and sediments, and sediment-water partitioning coefficients. Influential biological parameters will likely include organism dietary composition, body weight, and lipid content. Because of its influence on contaminant partitioning and on bioenergetic properties of growth and contaminant uptake, water temperature is also likely to be influential (Gobas and Arnot 2004).

The model has previously been parameterized to calculate uptake of PCBs in selected San Francisco Bay fish and wildlife (Gobas and Wilcockson 2002; Gobas and Arnot 2004). For the San Francisco Bay case study, the model will be reparameterized to other bioaccumulative organic contaminants on the Section 303(d) list of TMDL priority contaminants: DDTs, chlordanes, dioxins, and PBDEs (SFBRWQCB 2001). Parameterization and validation will be accomplished using extensive field data on concentrations of pesticides, dioxins, and brominated flame retardants in fish and wildlife (Davis et al. 2002; She et al. 2002; Greenfield et al. 2004). The model has previously been applied to predict PCB uptake in San Francisco Bay fish and wildlife. Target species modeled include sport fish with high trace organic contaminant concentrations (white croaker and jacksmelt), a forage fish likely to be consumed by wildlife (shiner surf perch), and several sensitive wildlife species (harbor seal, double crested cormorants, and Forster's tern) (Gobas and Arnot 2004). However, model parameters will also need to be developed for endangered species likely to have trophic linkages to San Francisco Bay (e.g., clapper rail, brown pelican, and least tern). Additional background information on San Francisco Bay is available in Davis (2004).

Newport Bay differs from San Francisco Bay in many respects; it is smaller, has different fish fauna, and is less complex in terms of sediment movement, salinity, and currents. The contaminant inputs to Newport Bay are also different from San Francisco Bay. Newport Bay has a large dataset on sediment and fish tissue concentrations, including a two-year study of fish tissue contamination of multiple recreational and forage fish species (Allen et al. 2004), and an evaluation of contaminant concentrations in several locations throughout the bay (Bay et al. 2004). Newport Bay therefore offers a good opportunity to evaluate the capability of the model to predict bioaccumulation from sediment contamination. For Newport Bay, the model will be applied to evaluate bioaccumulation of PCBs and DDTs, both of which have been sources of impairment in the bay. The model will be utilized to evaluate concentrations in both recreational fish species (e.g., spotted sand bass) and wildlife forage species (e.g., arrow goby and California killifish).

<u>Subtask 2.2. Select appropriate effects thresholds for case-study assessment.</u> As with the statewide sediment chemistry indicator development, the site-specific case studies must identify threshold tissue concentrations at which contaminants will pose adverse effects to fishes associated with the sediments, in addition to humans and wildlife that consume those fishes. These tissue concentrations would then be used to sediment chemistry thresholds based on the BSAFs developed in the mechanistic modeling.

Given the technical expertise required for effects threshold determination, and potential for controversy regarding appropriate endpoints, bioaccumulation study planning committee will be assembled. This committee will include representatives of agencies charged with protection of fish and wildlife (e.g., USFWS, CDFG), in addition to human health protection (e.g., USEPA and OEHHA). The committee will have several objectives: 1. confirm selection of appropriate target fish and wildlife species; 2. aid in evaluation of appropriate effects thresholds for protection of California biota; and 3. develop confidence and understanding by agency personnel regarding the indirect effects SQO development process.

Appropriate target species for the case studies will include the federally endangered estuarine fish and wildlife found in the study sites, Newport Bay and San Francisco Bay (Table 1). Three bird species fall into this category: California brown pelican (*Pelecanus occidentalis californicus*), California clapper rail (*Rallus longirostris obsoletus*), and California least tern (*Sterna antillarum browni*). Appropriate target species will also include fish species with strong benthic linkages identified in each location, and the federally listed Delta smelt and winter run Chinook salmon (Table 1). Based on field data and modeling indicating significant linkage to benthic food webs and bioaccumulation of hydrophobic organic contaminants, the target species in San Francisco Bay will also include white croaker and shiner surfperch (Table 1). Final species selection will be undertaken in coordination with local stakeholders during meetings with the bioaccumulation study planning committee and separate meetings, as needed. As discussed in Section 1.2, effects thresholds will be selected using current published studies and agency reviews (e.g., Beyer et al. 1996; PRC Environmental Management 1997; Canadian Council of Ministers of the Environment 1998; Brodberg and Pollock 1999; New York State Department of Environmental Conservation 1999).

<u>Subtask 2.3. Conduct model simulations, validation, and uncertainty analysis.</u> Given the large number of parameters that must be estimated, identification of influential parameters is often helpful in establishing future research priorities (MacLeod et al. 2002). This modeling exercise will include additional sensitivity analyses to explore the potential impact of confounding variables on model results, and identify parameters that strongly influence model results in each case study example. These analyses will be

based on Monte Carlo simulation, a widely used technique for evaluating the relative importance of various model inputs on results (e.g., McKone and Bogen 1991; Greenfield and Davis 2004). Simulations will then be conducted to evaluate the relative impact of sediment contamination versus other factors, including dietary variation, water contamination, and fish home range size. This will result in a probabilistic assessment of the likelihood of human and wildlife exposure at various sediment concentrations.

The model will be validated by comparing predicted BSAFs to BSAFs obtained using the empirical models discussed in Task 1. Specifically, field estimates of BSAF will be calculated using observed data on sediment and biota contamination and ancillary variables, and model results will be graphically and statistically compared to these estimates. This follows recent modeling of PCBs in San Francisco Bay fish and wildlife, in which validation demonstrated good correspondence between model predictions and actual observations (Gobas and Wilcockson 2002; Gobas and Arnot 2004) . It should be noted that in the case of endangered species, field data for model corroboration may not be available in some cases. If results indicate model bias or substantial error, other mechanistic model approaches may be undertaken. For example, models developed by Connolly and Thomann (Thomann 1989; Connolly 1991) could be applied, though additional parameterization to local conditions may be required.

<u>Subtask 2.4. Prepare report.</u> A technical report that describes the methodology and results from this task will be prepared. This document will include graphic presentation of simulation results, and a description of the modeling framework. This document will be made available to the SSC and other project participants for peer review and included in the Final Project Report.

Anticipated sediment chemistry indicator development and methods documentation

The extent to which the sediment chemistry thresholds developed in this project may be applied statewide (as opposed to requiring separate development for each individual water body) depends on the success of the empirical modeling efforts using statewide data. If it proves impossible to develop statistically significant relationships between sediment and biota contaminant concentrations, the project will conclude that models must be applied and validated on a case by case basis, for individual water bodies. If this turns out to be the case, statewide sediment chemistry thresholds for bioaccumulation protection would not be developed. Instead, the focus of the project would shift to providing detailed guidance, via the case study examples, for development of bioaccumulation-based sediment chemistry thresholds using local data collection and modeling.

Bioaccumulation-based sediment quality thresholds may be difficult to develop using preexisting empirical data sets. Therefore, it is necessary to develop project contingency plans, in the event that statistically significant empirical models are not obtained for specific contaminants. Table 2 presents three separate empirical modeling results, and the appropriate sediment chemistry indicator development and methods documentation. For a given contaminant, if there are no statistically significant empirical models for deriving BSAFs, the focus of the process will shift to mechanistic model development for specific case studies, and documentation of additional data needs for empirical model development and corroboration in additional sites.

Table 2. Modification of SQO development strategy and methods documentation based on varying empirical modeling results.

Results of Empirical Modeling	**Indicator Development**	**Methods Documentation**
Empirical relationships adequate* on a statewide basis	Set of statewide sediment chemistry indicator values	Describes how statewide indicators developed
Site-specific empirical relationships adequate*; statewide relationship not adequate	Set of sediment chemistry indicator values developed for individual water bodies having sufficient data	Focuses on method for establishing indicators for individual site; Describes additional data collection needs
Empirical relationships not adequate*	Individual waterbody sediment chemistry indicator values developed for mechanistic model case study examples only	Focuses on mechanistic model development and corroboration with empirical data

*adequate = models statistically significant and able to derive multiple threshold levels

Project Participants

This project is a multi-investigator collaboration. The San Francisco Estuary Institute is the lead agency responsible for the project. Ben Greenfield is the project manager and will receive technical assistance from Dr. Mike Connor, Dr. Jay Davis, Aroon Melwani, Meg Sedlak, and other SFEI staff, as needed. Additionally, Dr. Frank Gobas and Jon Arnot are participating as consultants on the project. Their efforts will focus on technical guidance and feedback regarding implementation of the site-specific mechanistic models. Steve Bay and Dr. Jim Allen, from SCCWRP, will help with parameter development for the Newport Bay case study. Dr. Bob Smith will provide statistical guidance on empirical model evaluation. Finally, Peggy Myre is assembling the datasets for the empirical exercise.

Schedule

Task	Activity or Deliverable	Completion Date
1: Evaluate Empirical Partitioning Models for Statewide Application	1.1. Develop dataset for empirical modeling 1.2. Select effects thresholds 1.3. Evaluate models 1.4. Prepare report	September 2004 December 2004 March 2005 August 2005
2: Apply a Mechanistic Bioaccumulation Model in Two Local Case Studies.	2.1. Parameterize model 2.2. Select effects thresholds 2.3. Conduct model simulations, validation, and uncertainty analysis 2.4. Prepare report	December 2004 January 2005 March 2005 August 2005

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