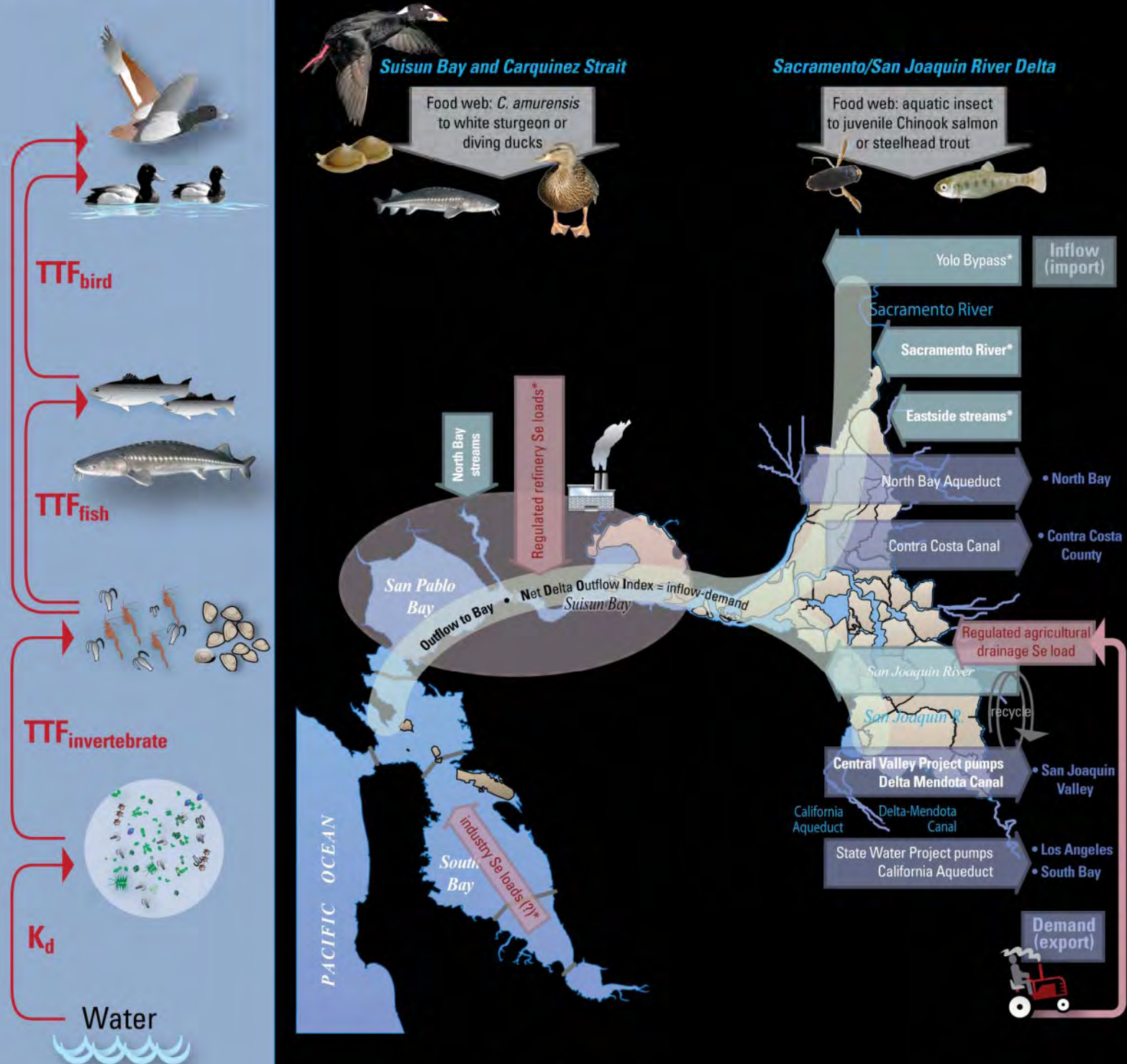


# Ecosystem-Scale Selenium Modeling in Support of Fish and Wildlife Criteria Development for the San Francisco Bay-Delta Estuary, California



Cover Art and Graphics: Jeanne DiLeo, USGS Office of Communications and Publishing, Menlo Park Publishing Service Center, Menlo Park, California.



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U.S. Geological Survey, Menlo Park, California

Administrative Report

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## Appendices (see separate files)

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Luoma, S.N., and Presser, T.S., 2009, Emerging opportunities in management of selenium contamination: Environmental Science and Technology, v. 43, no. 22, p. 8483-8487.

### Appendix B

Presser, T.S., and Luoma, S.N, 2010, A Methodology for Ecosystem-Scale Modeling of Selenium: Integrated Environmental Assessment and Management, v. 6, no. 4, p. 685-710 (plus Supporting Data, 32 p.).

### Appendix C

Selenium discharges from oil refineries (**Figures C1-C5**)

### Appendix D

Compilation of field data for the Bay-Delta (**Tables D1-D5**)

**Note:** A review by Coan (2002) concluded that the San Francisco Bay species *Potamocorbula amurensis* is now the genus *Corbula*, but the species name is still unclear. Because of this uncertainty, reference to the bivalve is now suggested as *Corbula (Potamocorbula) amurensis* (Thompson, 2005). However, we have used *Corbula amurensis* throughout this report.



# Ecosystem-Scale Selenium Modeling in Support of Fish and Wildlife Criteria Development for the San Francisco Bay-Delta Estuary, California

By Theresa S. Presser and Samuel N. Luoma

## Executive Summary

The San Francisco Bay-Delta Estuary (Bay-Delta) receives selenium (Se) internally from oil refinery effluents and externally through riverine agricultural discharges. Predator species considered at risk from Se (e.g., green and white sturgeon, scoter, scaup) consume the estuary's dominant bivalve, *C. amurensis*, an efficient bioaccumulator of Se. Recently proposed water-quality regulations for protection of the estuary require translating fish and wildlife tissue Se effect guidelines to dissolved Se concentrations. This change in regulatory approach requires consideration of intervening steps that 1) formally document system hydrology, biogeochemistry, biology, ecology, and ecotoxicology; and 2) quantitatively link ecosystem media (water, particulate material, and tissues of different food web species) as Se is processed through site-specific food webs. Such a methodology to predict site-specific ecological risk and derive Se criteria for the Bay-Delta would be the first regulatory action where a bioaccumulative element is managed to protect wildlife in a marine environment. Regulating seaward sites in the estuary also sets in motion consideration of upstream watershed sources.

For regulators and scientists, our approach offers an understanding that 1) diet drives protection and 2) the choice of food web and predator species is critical because the kinetics of bioaccumulation differs widely among invertebrates. Further, adequately characterizing the transformation of dissolved Se to particulate Se and the type and phase of the resulting particulate material quantifies the effect of Se speciation on both Se partitioning and Se exposure to prey through the base of the food web (i.e., particulate material to prey kinetics). Our approach also includes opportunities to analyze alternative modeling choices explicitly throughout the decision-making process.

Site-specific modeling for the Bay-Delta includes derivation of: 1) salinity-specific operationally defined factors for partitioning of Se between water and suspended particulate material ( $K_{ds}$ ); 2) dietary biodynamic Trophic Transfer Factors (TTFs) for important food web inhabitants; 3) seasonal scenarios that illustrate hydrologic conditions, life-cycles of predator species, exposure cycles, and habitat use; and 4) species-specific effect guidelines. Effect guidelines for species at risk in the Bay-Delta were provided by the U.S. Fish and Wildlife Service (USFWS). Effect guidelines are explicit to exposure route (e.g., maternal), endpoint (e.g., hatchability) and magnitude of effect realized (EC0, EC05, and EC10) to address regulatory considerations for the U.S. Endangered Species and Migratory Bird Treaty Acts. Knowing the details of an at-risk predator's location during critical life stages for Se effects allows correlating trends in diet and exposure that occur in the estuary. Thus, our approach uses a mechanistic biodynamic basis to quantify transformation and bioaccumulation as a foundation for criteria development and site-specific data for food webs, life cycles, habitat use, and effects to set choices in modeling scenarios.

We employ both a salinity-specific transect approach, encompassing tidally-influenced sites across the Bay-Delta from near Chipps Island to the Golden Gate Bridge, and a geographically focused approach encompassing Suisun Bay and Carquinez Strait. The most recent transect data (i.e., matched datasets for dissolved and suspended particulate material) from 1997-1999 are used for modeling a seaward *C. amurensis*-based food web. Similarly, the most recent transect data from 2003-2004 are used for modeling a landward aquatic insect-based food web. Transect sampling from the 1990s represents wet and above normal years in both low flow and high flow seasons. Transect sampling from the 2000s represents above normal and below normal years in both low flow and high flow seasons.

Profiles across the estuary within a series of specified freshwater residence times (e.g., June, 1998, 11 days; November, 1999, 70 days) show the range of dissolved Se concentrations is narrowly defined as 0.070-0.320  $\mu\text{g/L}$ . The profiles of suspended particulate material Se concentrations show a less narrow definition with a range of 0.15-2.2  $\mu\text{g/g}$  dry weight. In the more restricted approach used for Suisun Bay-Carquinez Strait that eliminates freshwater and ocean interfaces, the range of dissolved Se concentrations is 0.076-0.215  $\mu\text{g/L}$ , with the range of suspended particulate material Se concentrations as 0.15-1.0  $\mu\text{g/g}$  dry weight.

$K_{ds}$  are the derived ratios of dissolved and suspended particulate material Se concentrations from transect sampling across the estuary. The operational  $K_{ds}$  used here quantify the complex process of transformation to represent exposure and bioavailability at the base of the food web. The profiles of  $K_{ds}$  across the estuary illustrate the range in biogeochemical transformations and their patterns as flow conditions change. Generally,  $K_{ds}$  vary similarly as suspended particulate material Se concentrations across transects because of the narrowly defined range of dissolved Se concentration. Specifically, patterns during high flow conditions in April, 1999 and low flow conditions in November, 1999 are distinctly different. As residence time increases from 16 days in April to 70 days in November, the profile shape moderates and a hydrodynamic span of efficient transformation is identified. The range for the Bay-Delta continuum is 712-26,912, with mean  $K_{ds}$  shown to increase with increasing residence time.  $K_{ds}$  selected for use in modeling scenarios range from 3,198 to 7,614. The  $K_d$  range selected when the modeling location is limited to Suisun Bay-Carquinez Strait is 1,180-5,986.

The range of derived  $\text{TTF}_{C. amurensis}$  is 14-26 for local conditions, an increase when compared to a laboratory-derived mean value of 6.25.  $\text{TTF}_{\text{insect}}$  and  $\text{TTF}_{\text{bird egg}}$  are not site-specific, but are selected from literature values ( $\text{TTF}_{\text{insect}} = 2.8$ ;  $\text{TTF}_{\text{bird egg}} = 2.6$ ). For  $\text{TTF}_{\text{fish}}$ , both a literature value of 1.1, and in the case of white sturgeon, a field-derived TTF of 0.8 are used.

Validation of the model shows the model is able to generate 1999-2000 seaward conditions for Se concentrations in a *C. amurensis* to white sturgeon food web and 2003 landward conditions for Se concentrations in an aquatic insect to largemouth bass food web. Thus, the model is able to 1) quantify transformation and biodynamics processes for the estuary and its food webs; and 2) predict that food webs dependent on *C. amurensis* are the most sensitive to Se inputs, provide the most Se exposure, and are highly vulnerable.

Modeling to protect sturgeon and clam-eating bird species is based on consumption of the clam *C. amurensis*, an invertebrate that bioaccumulates Se approximately twenty-fold that of the concentration in suspended particulate material (i.e.,  $\text{TTF}_{C. amurensis} = 17$ ). Modeling to protect juvenile Chinook salmon and steelhead trout is based on consumption of aquatic insects, an invertebrate that bioaccumulates Se approximately three-fold that of the concentration in suspended particulate material (i.e.,  $\text{TTF}_{\text{insect}} = 2.8$ ). The model also addresses an alternative dietary preference by predators: a mix of invertebrate species (i.e., a 50% *C. amurensis* and 50% amphipod diet generates a  $\text{TTF}_{\text{mixed}}$  of 8.8).

Allowable dissolved, particulate, and prey Se concentration calculated through modeling of a specified predator species are based not only on the dietary TTF for that species (i.e., exposure), but also

on the toxicological sensitivity inherent to the predator (i.e., effects guideline provided by the USFWS for species at risk in the estuary). Hence, bioaccumulation in salmonids will be less than that in sturgeon because of dietary preference, but toxicity guidelines for salmonids are lower due to increased toxicological sensitivity. In this case, the predicted allowable dissolved Se concentration is a value that is a mathematical combination of the influences of the lower dietary TTF and the higher toxicological sensitivity.

Illustrated scenarios using a set of specific guidelines and modeling choices from the range of temporal hydrodynamic conditions, geographic locations, foodwebs,  $K_d$ , and TTFs described above, bound allowable dissolved, particulate, and prey Se concentrations. Consideration of compliance with allowed Se concentrations across media (i.e., water, particulate, prey, and predator) harmonizes regulation and is a measure of ecological consistency and relevance of the links among exposure, transfer, and effects. The specificity of these scenarios demonstrates that enough is known about the biotransfer of Se and the interconnectedness of habitats and species to set a range of limits and establish an understanding of the conditions, biological responses, and ecological risks critical to management of the Bay-Delta.

Analysis of dissolved, suspended particulate material and *C. amurensis* Se concentrations and  $K_d$ s for Suisun Bay-Carquinez Strait as a function of freshwater residence time (11, 16, 22 and 70 days) shows that critical ecological times are functionally connected to the underlying dynamics and processes of low flow periods. Transformation of dissolved Se to suspended particulate material Se (i.e., dissolved Se decreases as suspended particulate material Se concentrations increases) occurs in the estuary as flow slows down. *C. amurensis* Se concentrations also increase with increasing residence time, as does the presence of a majority of particulate organo-Se within a residence time of 22 days. Given the steepness of these curves, regulation of suspended particulate material Se concentration may be a more sensitive parameter on which to assess change and choice. Defining or conceptualizing a baseline dissolved Se concentration or condition for the estuary is less certain because of the small dynamic range of dissolved Se concentrations.

Predictions from modeling scenarios show that choices of geographic constraints, species, diet, and estuary conditions all are influential in risk management for Se. Thus, the more specificity added to the model, the less uncertainty in predictions. If, for example, the geographic range is narrowed by using data only from Suisun Bay, then freshwater and ocean interfaces are avoided. If the temporal range is narrowed to low flow seasons of dry years, then focus can be on times when the transformative nature of the estuary is elevated. Juxtaposition of times when prey species achieve maximum Se concentrations and critical life stages of species at risk are present allows focus of regulatory considerations on times that govern Se's ecological effects (i.e., *ecological bottlenecks*).

Further refinements to the approach would include consideration of: 1) contributions of Se source riverine end-members; 2) hydrodynamic relationships of riverine and internal Se sources to Se concentrations in the estuary (i.e., an Se budget through the estuary); 3) processes at the interfaces of freshwater/bay/ocean; 4) collection of current temporally and spatially matched Se datasets for water, suspended particulate material, and food web species; and 5) further linkage of ecosystem-scale modeling to fine structure estuary processes. Analysis of Se concentration and speciation for characterized particulate phases are practical measures of the complex water/sediment/particulate *milieu* that forms the base of the food web and is consumed as food by invertebrates. Hence, future monitoring to increase the suspended particulate material database under a suite of flow conditions would enhance our understanding of estuarine transformation. Monitoring invertebrate Se concentrations in food webs also is a practical, informative step in monitoring because the first and second most variable aspect of Se dynamics (i.e.,  $K_d$  and  $TTF_{\text{invertebrate}}$ ) are integrated into invertebrate bioaccumulation.

In particular for modeling of avian species, uncertainties exist around laboratory-derived biodynamic modeling parameters; movement and migration; and links of diet and tissue Se concentrations under site-specific conditions (i.e., field-derived  $TTF_{\text{bird egg}}$ ). Additionally, modeling of overwintering clam-eating migratory bird species, such as scoter and scaup, based on potential chronic Se effects that may impact staging would assess these species in scenarios relevant to their use of the estuary. Chronic toxicity effects include:

- compromised body condition (low body mass);
- oxidative stress (increased susceptibility to disease as immune system is suppressed);
- decreased winter survival;
- decreased reproductive fitness (decreased breeding propensity, reduced recruitment) and;
- behavioral impairment (missed breeding window, delayed timing of departure).

Predictions from a reference dose methodology for birds also would strengthen outcomes for protection of avian species.

The methodology used here is able to document estuary and ecosystem fine-structure processes and provide the basis and context for future scenario development. The greatest strength of the analytical and modeling processes is that it is an orderly, ecologically harmonized derivation approach for assessing different choices of criteria for protection of fish and birds. Collection of modern data and additional modeling in collaboration with the final development of criteria would test if identified mechanisms and derived factors are applicable to the Bay-Delta of today. Further modeling also would provide decision-makers with additional choices based on specific questions that arise during collaborative discussions.

## Introduction

Aquatic-dependant wildlife are unprotected under national aquatic life water quality criteria for Se, but these criteria are currently being revised [U.S. Environmental Protection Agency (USEPA), 1992; 2004]. National freshwater water quality Se criteria (5  $\mu\text{g/L}$  chronic and 20  $\mu\text{g/L}$  acute) for the protection of aquatic life are directed at protection of fish and are based on field data for effects in fish at Belews Lake (USEPA, 1987). National water quality Se criteria for the protection of marine aquatic life allow a maximum concentration of 290  $\mu\text{g/L}$  and a continuous concentration of 71  $\mu\text{g/L}$ , concentrations approximately an order of magnitude higher than freshwater criteria. What evidence is available from estuarine environments suggests that these guidelines are seriously under-protective for at least some predator species (Luoma et al., 1992; Presser and Luoma, 2006; Luoma and Presser, 2009).

Consideration of development of Se criteria specific to wildlife began in 1989 as an outcome of the ecological disaster at Kesterson National Wildlife Refuge, California, where aquatic birds experienced death and deformity (Presser and Ohlendorf, 1987; USEPA, 1989). The U.S. Clean Water Act (1972) provides the legal authority for deriving water quality criteria for the protection of aquatic life, wildlife, and human health. USEPA in 1985 developed methodologies for deriving water quality criteria that included protection of wildlife under determination of a Final Residue Value (FRV) (USEPA, 1985). A USEPA revision of criteria for the Great Lakes System [Great Lakes Initiative (GLI), USEPA, 1995] deleted the FRV method and applied a new methodology for contaminants and wildlife. Since that time, the GLI methodology has been applied to DDT, PCBs, and mercury on a Great Lakes-specific basis for piscivorous birds and mammals. As an outgrowth of the GLI methodology, Petersen and Nebeker (1992) proposed a freshwater waterborne Se threshold estimate for protection of aquatic-dependent birds and mammals. Skorupa and Ohlendorf (1991) proposed a range of waterborne

Se concentrations for the protection of nesting aquatic birds through use of field-derived regressions of food web and avian uptake.

Adjustments to the development of Se criteria specifically for California were called for by 1) the USEPA through the National Toxics Rule (NTR) and the California Toxics Rule (CTR) (USEPA, 1992; 2000); and 2) the USFWS and National Marine Fisheries Service (NMFS) through their Biological Opinion (USFWS and NMFS, 1998 and amended, 2000). In general, these adjustments were necessary to consider 1) the bioaccumulative nature of Se in aquatic systems; 2) Se's long-term persistence in aquatic sediments and food webs; 3) the importance of dietary pathways in determining toxicity; and 4) protection of threatened and endangered species.

Specifically, pursuant to section 7(a) of the U.S. Endangered Species Act (ESA) (1973), the USEPA consulted with the USFWS and NMFS concerning USEPA's rulemaking action for California. USEPA submitted a Biological Evaluation for their review as part of the consultation process in 1994. This evaluation found that the proposed CTR was not likely to jeopardize the continued existence of any federally listed species or result in the destruction or adverse modification of designated critical habitat. In April of 1998, the Services sent USEPA a draft Biological Opinion that found that USEPA's proposed rule would jeopardize federally listed species. After discussions with the USFWS and NMFS, the USEPA agreed to several changes in the final rule and USFWS and NMFS, in turn, issued a final Biological Opinion finding that USEPA's action would not likely jeopardize the continued existence of federally listed species. The agencies agreed that federally listed fish and wildlife species that are aquatic system foragers would be protected under future criteria and procedures for site-specific adjustments.

To achieve these goals and as part of the remedy for these problems, the USEPA initiated an interagency project with the USFWS and the U.S. Geological Survey (USGS) to address issues of 1) a methodology for translation of a tissue guidelines to protective site-specific dissolved Se concentrations (implementation of tissue criteria); 2) inclusion of protection of wildlife species (i.e., federally listed species) in regulatory methodologies; and 3) site-specific criteria development for the Bay-Delta (USEPA, 1999).

A methodology for ecosystem-scale modeling of Se is now available (see **Appendices A and B**, Luoma and Presser, 2009; Presser and Luoma, 2010). Analysis from this biodynamically-based methodology showed, in general, that:

- a crucial factor ultimately defining Se toxicity is the link between dissolved and particulate phases at the base of the food web (i.e.,  $K_d$ );
- collection of particulate material phases and analysis of their Se concentrations are key to representing the dynamics of the system;
- bioaccumulation in invertebrates is a major source of variability in Se exposure of predators within an ecosystem, although that variability can be explained by invertebrate physiology (i.e.,  $TTF_{\text{invertebrate}}$ );
- $TTF_{\text{fish}}$  is relatively constant over the range of species considered here; and
- Se concentrations are at least conserved and usually magnified at every step in a food web.

Here, we specifically adapt this methodology to the conditions and food webs of the Bay-Delta and present ecosystem-scale Se modeling in support of fish and wildlife criteria development for the estuary.

# San Francisco Bay-Delta Estuary

## Regulation

Habitats in California important to consider for site-specific Se criteria development include the Bay-Delta and its watersheds (Presser and Luoma, 2006) (**Figure 1**). In 1992, USEPA found that the utilization of the saltwater Se criteria for the Bay-Delta would be inappropriate and promulgated the current national chronic freshwater selenium criteria for the Bay-Delta (USEPA, 1992; 2000). USEPA also reserved the acute freshwater aquatic life criterion for Se (USEPA, 2000). In doing so, USEPA disapproved the statewide Se objective for the Bay-Delta on the basis that there was clear evidence that the objective would not protect the designated fish and wildlife uses (USEPA, 2000). For example, the California Department of Health Services had issued waterfowl Se consumption advisories and scientific studies had documented Se toxicity to fish and wildlife (USEPA, 2000; Presser and Luoma, 2006). The USEPA also re-stated its commitment to object to National Pollutant Discharge Elimination System (NPDES) permits issued for the estuary that contained effluent limits based on objectives greater than the freshwater criteria of 5 µg/L (four day average) and 20 µg/L (1 hour average).

## Setting

The Bay-Delta, the largest estuary on the west coast, has been described as the *urbanized* estuary because of the extensive modification of its marshlands and the hydrologic systems that feed it (Conomos et al., 1979; 1985; Nichols et al., 1986). Two major rivers, the southward flowing Sacramento and the northward flowing San Joaquin, join at the Delta, with seawater entering through the Golden Gate Bridge (**Figure 1**). The generalized schematic of the estuary (**Figure 1**) shows the locations of:

- Sacramento River;
- San Joaquin River;
- Delta (nominally upstream of Chipps Island);
- North Bay (Suisun Bay, Carquinez Strait, San Pablo Bay);
- Central Bay;
- Pacific Ocean at the Golden Gate Bridge; and
- South Bay.

The major portion of the estuary from the rivers to the Golden Gate Bridge is termed the Northern Reach. The North Bay and the Delta are emphasized here as areas for criteria development. The South Bay is not a focus here. Although similar concepts apply, the South Bay can be modeled separately because it receives source inputs from a different watershed than the Northern Reach (**Figure 1**). However, waters do exchange and similar estuarine processes, habitats, and inhabitants do occur within all segments of the estuary.

## Selenium Sources

Current major sources of Se to the Bay-Delta (**Figure 2**) are:

- irrigation drainage from seleniferous agricultural lands of the western San Joaquin Valley conveyed through the San Joaquin River; and
- oil refinery wastewaters from processing of seleniferous crude oils at North Bay refineries.

Regulation of Se for oil refiners is occurring through water quality Se criteria promulgated by USEPA for the Bay-Delta (USEPA, 1992; 2000) and limits on loads and concentrations enacted by the state in



1992 [San Francisco Bay Regional Water Quality Control (San Francisco Bay Board), 1992 a,b; 1993; 2010] (**Figure 3**). The five refineries located in the North Bay and their discharge locations are: Chevron Refinery at Richmond, discharge to San Pablo Bay; Martinez (Shell) Refinery at Martinez, discharge to Carquinez Strait; Tosco (Conoco Phillips) Refinery at Rodeo, discharge to San Pablo Bay; Tesoro Golden Eagle Refinery at Martinez, discharge to Suisun Bay; Valero Refinery at Benicia, discharge to Suisun Bay. A compilation of refinery Se loads from 1986-2009 is shown in **Table 1** (San Francisco Bay Board, 1992a,b; 1993; Lila Tang and Johnson Lam, San Francisco Bay Board, personal communication, 1999-2006; USEPA, 2010) and recent Se data are displayed in **Appendix C, Figures C1-C5**. Previous refinery mass emissions were reduced by 75% (cumulative reduction from baseline of 4,936 lbs during 1989-1991) (San Francisco Bay Board 1992a,b; 1993). Proposed load reductions were achieved in 1998 and since then, the combined Se load from the refiners has remained at approximately 1,200 pounds (lbs)/year. The target of 1,234 lbs/year was a balance between ecological, technological, and economic considerations. An iterative mass emissions strategy was used in lieu of site-specific water quality objectives because water-column Se concentrations were considered not predictive of Se bioaccumulation (San Francisco Bay Board, 1993). Daily water-column Se concentrations in effluents were as elevated as 300 µg/L before 1998, but allowed daily maximum effluent limits now are within the range of 34-50 µg/L. Discharger's outflows are designed to achieve a minimum initial dilution of 10:1, but the range of estimated initial dilutions is 15:1-200:1 (San Francisco Bay Board, 2009; 2010). Dilution credits of 8:1 and 10:1 are in-place, with an average daily flow range of 1.9-7.4 million gallons/day. The range of allowed average effluent Se limits is 0.85-2.0 lbs/day.

Regulation of Se for the agricultural community of the Grassland Drainage Area is occurring through the Grassland Bypass Project (**Figures 3 and 4**). The project was initiated in 1996 and is for use of the San Luis Drain and the tributaries of the San Joaquin River for discharge of agricultural drainage from approximately 100,000 acres of land [U.S. Bureau of Reclamation (USBR), 1995; 2001]. As noted below, the amount of agricultural Se load discharged to the Bay-Delta depends on the amount of San Joaquin River flow that is allowed to enter the Bay-Delta and how much is recycled back to the south (Presser and Luoma, 2006) (**Figure 2**).

Historical and current Se loads from the Grassland Bypass Project measured where the San Luis Drain discharges into a tributary of the San Joaquin River (i.e., Mud Slough) are shown in **Figure 3**. The use agreement for the project was re-negotiated in 2001 and was to end in 2010 with zero discharge. However, the project did not meet its goals and is now being re-negotiated to continue through 2020 (USBR and San Luis and Delta-Mendota Water Authority, 2009). Although dependent on water-year type, compliance with Se load targets gradually reduces the amount of Se allowed for discharge into the San Joaquin River (**Figure 4**). For example, the Se load measured at the compliance point (i.e., the San Luis Drain at Mud Slough) was 7,096 lbs in 1998; 5,023 lbs in 2003; 4,286 lbs in 2005; 3,301 lbs in 2008; and 1,239 lbs in 2009 (**Figure 4**). Imposition of more restrictive Se targets for the San Joaquin River is balanced by shifting a percentage of the generated annual drainage Se load to storage in groundwater aquifers and lands designated for disposal (San Francisco Estuary Institute, 2004-2005). For example, drainage control activities resulted in storage of 4,200 lbs Se within the Grassland Drainage Area in 2005. For proposed targets from 2009-2019, wetter years allow greater discharge (e.g., 4,480 lbs Se/year during 2009-2014) than drier years (**Figure 4**). Proposed targets continue to ramp down in the coming years with ultimate goals ranging from 150-600 lbs/year by 2019 (**Figure 4**). The long-term ecological consequences of such a shift in environmental compartments and increased storage of Se within the existing Se reservoir in the San Joaquin Valley is currently under debate (Presser and Schwarzbach, 2008). However, data for the Grassland Bypass Project area show Se is accumulating to levels in bird eggs of black-necked stilt, American avocet, and killdeer that far

exceed threshold Se concentrations for impairment of reproduction (San Francisco Estuary Institute, 2004-2005; H.T. Harvey and Associates, 2004-2009).

Restoration of the San Joaquin River is proceeding under a comprehensive program with many environmental goals such as increasing flows in the upper reaches of the river to re-establish salmon runs in the river (Natural Resources Defense Council and others, 1988, 1989, 1992, 1999; San Joaquin River Group, 2010). Also, regulation of salinity for the San Joaquin River is taking place at Vernalis and three locations interior to the southern Delta (California State Water Resources Control Board, 1999). Few data are available to quantify a San Joaquin River end-member Se concentration at the head of the estuary. Dissolved Se concentrations for the San Joaquin River averaged 0.71  $\mu\text{g/L}$  (range 0.40-1.07  $\mu\text{g/L}$ ) at Vernalis during wet year and above normal conditions in 1998-1999 (Cutter and Cutter, 2004).

Discharge of Se to the Sacramento River is unregulated. Again, few data are available to quantify a Sacramento end-member Se concentration at the head of the estuary. Dissolved Se concentrations in the Sacramento River averaged 0.07  $\mu\text{g/L}$  (range 0.05-0.11  $\mu\text{g/L}$ ) at Freeport during wet year and above normal conditions in 1998-1999 (Cutter and Cutter, 2004). Other unregulated sources of Se include 1) effluents from wastewater treatment plants and industries other than refineries; and 2) discharges from watersheds that drain directly into the estuary.

Restoration of the estuary also is underway. The Delta Regional Ecosystem Restoration Implementation Plan (DRERIP) is focusing on construction of conceptual models that describe the processes, habitats, species, and stressors of aquatic environments of the estuary (<http://www.dfg.ca.gov/delta/erpdeltaplan/>). The models will be interconnected and used to help evaluate future restoration actions.

## Hydrodynamic Connections

A current detailed Se budget or mass balance of Se as a function of source and conveyance is not available for the Bay-Delta. Riverine inputs as they mix with seawater and internal Se sources determine Se concentrations in the Bay. Seasonal and year-to-year variations in discharges from rivers, streams, and anthropogenic sources influence dissolved Se concentrations in the Delta and estuary (Presser and Luoma, 2006). The Sacramento and San Joaquin Rivers are the main sources of inflow, with the Sacramento River being the dominant inflow under current management conditions. The Sacramento River dilutes the more concentrated Se inputs from other sources.

Parameters critical in determining the balance of water and Se inputs for the Bay-Delta are:

- total river (Sacramento River and San Joaquin River) inflow;
- water diversions or exports (i.e., pumping at Tracy and Clifton Court Forebay south to the Delta-Mendota Canal and the California Aqueduct);
- proportion of the San Joaquin River directly recycled south before entering the estuary; and
- total outflow of the estuary to the Pacific Ocean or Net Delta Outflow Index (NDOI).

NDOI is essentially inflow minus demand (USBR, 2010) (**Figure 2**). NDOI is related to residence time for freshwater in the Bay-Delta (Cutter and Cutter, 2004) and, hence, to processes that affect Se transformations within flow seasons of a water year and within types of water years (Presser and Luoma, 2006). Water years begin on October 1<sup>st</sup> and are classified here based on Sacramento Valley unimpaired runoff (<http://cdec.water.ca.gov/cgi-progs/iodir/WSIHIST>). Maximum discharge from the rivers is during January-February and minimum discharge is during July through August (Conomos et al., 1979; 1985; Peterson et al., 1985; Presser and Luoma, 2006).

Flow, and thus freshwater residence time, vary dramatically during the year as water management and diversions take place (<http://www.usbr.gov/mp/cvo/>; Enright and Culberson, 2010)

(**Figure 3**). Processes such as phase transformation and uptake by prey depend on, to some extent, the hydrodynamics of the estuary (Meseck and Cutter, 2006; Presser and Luoma, 2006; Tetra Tech Incorporated, 2010). Residence time, seasonal period (low flow and high flow), and water year type (critically dry, dry, below normal, normal, above normal and wet) can be used to categorize modeling scenarios (see later discussion).

## Overview of Modeling

Used optimally, the modeling approach provided here is a tool to frame a site-specific ecological occurrence of Se exposure; quantify exposure within that ecosystem; and narrow uncertainties about how to protect it by understanding the specifics of the underlying system ecology, biogeochemistry, and hydrology (Luoma and Rainbow, 2005; Luoma and Presser, 2009; Presser and Luoma, 2010). With this approach, it is possible to differentiate consumer species and their food webs in terms of bioaccumulative potential and predict overall ecological risk. Specifically, modeling in support of development of wildlife Se criteria for the Bay-Delta is through adaptation of the San Francisco Bay-Delta Selenium Model (Luoma and Presser, 2000; Presser and Luoma, 2006) (**Figure 5**) and the Ecosystem-Scale Selenium Model (Luoma and Presser, 2009; Presser and Luoma, 2010) (**Figure 6**).

The linked factors that determine the effects of Se in ecosystems and the data needs for modeling and understanding these linkages are shown in **Figure 6**. The organizing principle for the methodology is the progressive solution of a set of equations or models, each of which quantifies a process important in Se exposure (**Figure 7**). **Table 2** compiles the generalized steps used to translate a predator tissue Se concentration guideline to a dissolved Se concentration. The ecotoxicology of Se and the specific effects of Se on fish and birds are shown in **Figure 8**. Reproductive effects are key in Se's actions, but chronic effects also are expressed. Modeling and prediction thus enables quantifying Se toxicity under different management or regulatory proposals.

Modeling is used to quantify the environmental concentrations and conditions that would result from a pre-determined Se concentration in the tissues of a predator. Assuming the tissue guideline is generic for all fish or birds, the choice of the predator species in which to assess that concentration is still important because it determines the food web invertebrate species (**Figure 6**). That specific predator's feeding habits drive the choice of invertebrate, for which a species-specific transfer factor (i.e., TTF) connects an invertebrate Se concentration to a suspended particulate material Se concentration that is the source of food for the invertebrate. An environmental partitioning factor (or a range of factors) for partitioning of Se between water and suspended particulate material ( $K_d$ ) feasible for that ecosystem is then used to determine the *allowable* water-column concentration, which is ultimately the concentration in that specific type of environment and food web that would result in the specified Se concentration in the predator (i.e., the applied criterion). Thus, the *allowable* water column concentration can differ among environments; an outcome that reflects the realities of nature. This biologically explicit approach also forces consideration of the desired uses and benefits in a watershed (i.e., which species of birds and fish are the most threatened by Se or are the most important to protect). To translate exposure into toxicity here, we employ species-at-risk for the Bay-Delta (e.g., sturgeon and salmonids) and their effect guidelines provided by the USFWS (see later discussion).

**Figure 2** illustrates some of the complexities that need to be addressed in developing a site-specific approach for an estuary affected by several Se sources (i.e., internal oil refinery and watershed agricultural drainage) and supporting different food webs associated with a gradient of salinities. For example, agricultural Se loading is through the San Joaquin River into the Delta where food webs are modeled as aquatic insect-based. Yet, Se loading through the Delta affects the Bay and adds to oil refinery Se loads where food webs are modeled as *C. amurensis*-based. The North Bay, where *C.*

*amurensis* is the dominant bivalve species and is a strong Se bioaccumulator, is the most affected by Se loading (Stewart et al., 2004; Presser and Luoma, 2006) (**Figure 2**). Hence, overall, tracking and differentiation of Se sources is an important component of management for the estuary, especially as changes to the hydrologic configuration of the Delta (e.g., the amount of Sacramento River and San Joaquin River allowed to enter the Bay) are considered in the future.

**Figure 9** shows site-specific processes and parameters for the Bay-Delta and acts as a roadmap through the modeling process detailed in the sections below. The approach for the estuary is through specified food webs, locations, and flow seasons in modeling scenarios. Detailed model steps, parameters, and derivations are illustrated for a seaward *C. amurensis* food web and a landward aquatic insect food web (**Figure 9**). A spatial component for modeling is based on a salinity gradient across the estuary or on a particular portion of the estuary (i.e., Suisun Bay). A temporal component for modeling addresses the effect of water-year type and within that type, a flow season (low flow, nominally June through November; high flow, December through May). Addition of a temporal component based on residence time further delineates a fine-scale approach, as do the additions of details of species life cycles and habitat use. The more detailed the modeling choices or approach, the less uncertainty there is in the forecasts. As illustrated (**Figure 9**), the main considerations used here for a site-specific Bay-Delta approach are:

- species-specific effects guidelines to quantify regulatory concerns;
- food webs to define the choice of prey and predator pairs (i.e., TTFs);
- salinity to constrain locations and thus potential pathways for loading, transformation, and exposure;
- flow seasons to connect to hydrology, predator life cycles, and habitat use; and
- residence time to further constrain transformation and biodynamic processes.

Thus, a formalized approach captures both mathematical components and exposure gradients over time. A focused area approach would enable regulatory consideration of sources or impacted downstream areas.

## Fish and Wildlife

### Species at Risk

The USFWS (2008) provided a comprehensive list of species for evaluation of Se exposure risk in the Bay-Delta (**Table 3**). They stated that 1) aquatic dependent species feeding directly in the benthic food web of the Bay-Delta were considered at greater risk to Se exposures than those feeding in the pelagic/planktonic food web; and 2) exposure assessment was based on a) dependence on a benthic food web, b) population status, and c) sensitivity to Se. The list included 27 bird species, 15 fish species, the salt marsh harvest mouse, the giant garter snake, and the Dungeness crab. The species listed in **Table 3** then were narrowed to provide a list of species considered most at risk (**Table 4**). Species most at risk from Se in the Bay-Delta and their status (federal/state) include:

- bald eagle (*Haliaeetus leucocephalus*): delisted, U.S. Migratory Bird Treaty Act (MBTA), Bald and Golden Eagle Protection Act (BGEPA)/protected, endangered;
- California clapper rail (*Rallus longirostris obsoletus*): endangered/protected, endangered;
- greater scaup (*Aythya marila*): MBTA/none;
- lesser scaup (*Aythya affinis*): MBTA/none;
- white-winged scoter (*Melanitta fusca*): MBTA/none;
- surf scoter (*Melanitta perspicillata*): MBTA/none;

- black scoter (*Melanitta nigra*): MBTA/none;
- Chinook salmon (*Oncorhynchus tshawytscha*): endangered, threatened/endangered, threatened;
- steelhead (*Oncorhynchus mykiss*): threatened/none;
- green sturgeon (*Acipenser medirostris*): threatened/concern, fishing prohibited;
- white sturgeon (*Acipenser transmontanus*): none/limited fishing;
- Sacramento splittail (*Pogonichthys macrolepidotus*): concern/threatened; and
- giant garter snake (*Thamnophis gigas*): threatened/threatened.

Although its diet does not include bivalves, Delta smelt (*Hypomesus transpacificus*) is a threatened species that is endemic to the estuary and, hence, is considered by the USFWS (2008) as threatened overall. A reptile species (USFWS, 2006, 2009a) and an invertebrate species USFWS (2008) also are documented as important inhabitants of the estuary. The threatened giant garter snake (*Thamnophis gigas*) inhabits the Delta Basin and watershed valleys (USFWS and NMFS, 1998; amended 2000; USFWS, 2006). This species is an aquatic predator that feeds on small fish and larval/sub-adult frogs (USFWS, 2009a). The estuary is a nursery for the ocean-breeding, bottom-feeding Dungeness crab (*Cancer magister*). This species consumes *C. amurensis*, but invertebrates, in general, are known to have lower toxicological sensitivity (Presser and Luoma, 2006). However, Dungeness crab may serve to further biomagnify Se by providing an additional trophic transfer step (i.e., *C. amurensis* to Dungeness crab to large predator fish or mammals).

## Effects and Effect Levels

Effects of concern for Se in fish and wildlife (**Figure 8**) are:

- reproductive effects
  - birds: hatchability, teratogenesis, chick survival and growth; and
  - fish: deformity, larva and fry survival and growth
- chronic effects.

Species-specific effect models developed as part of the DRERIP process are shown for diving ducks, sturgeon, and salmonids inhabiting the Bay-Delta (**Figure 10**, adapted from DRERIP Selenium Model, Presser, et al., in review). These effects can lead to changes within ecosystems including population reductions, loss of species or individuals, and community changes.

The USFWS (2009b) provided Se effect guidelines and associated levels of protection (e.g., EC10 for birds is the Se concentration in eggs associated with a 10% reduction in hatchability) for predator species at risk in the estuary based on several different toxicity endpoints (**Table 5**). [Note: Technically, the term EC10 does not apply to quantitative reproductive performance endpoints. The proper term to apply to quantitative reproductive performance endpoints such as 10% reduction in egg hatchability is IC10 (or 10% Inhibition Concentration). However, the subtle conceptual distinction between these two technical terms has not been recognized in the avian toxicology literature for Se; therefore, we conform with the common use of the term EC10 with reference to avian egg hatchability and simply note here that we are aware of this issue (see Environment Canada, 2005)]. Data from the study of toxicity in mallards is used when modeling clam-eating bird species in the estuary because these are the most comprehensive studies available. The effect guideline ranges derived for tissue and diet in dry weight (dw) are:

- mallard (egg 2.8-7.7; diet 2.3-5.3 µg/g dw);
- adult female white sturgeon (whole-body 7.0-8.1 µg/g dw; diet 26-32 µg/g dw);
- juvenile white sturgeon (diet 0.95-1.6 µg/g dw);
- juvenile Chinook salmon (whole-body 1.0-1.8 µg/g dw; diet 1.5-2.7 µg/g dw);

- juvenile rainbow trout (whole-body 1.3-2.2 µg/g dw; diet 2.4-5.0 µg/g dw); and
- larval rainbow trout (diet 0.31-1.6 µg/g dw).

**Table 6** gives generic guidelines for Se effect concentrations also developed by the USFWS (USFWS, 2005; 2009b; Skorupa, et al., 2004; Skorupa, 2008). A subset of the effects guidelines and associated levels of protection shown in **Tables 5 and 6** are used in modeling to predict toxicity under different regulatory proposals. Emphasis here is on illustration of Se exposure for juvenile white sturgeon, diving ducks as represented by the mallard, and juvenile Chinook salmon.

## Estuary Food Web and Exposure Models

Conceptual models for the estuary show clam-based food webs for seaward sites and aquatic insect-based food webs for landward sites (**Figures 2 and 11**). The *C. amurensis*-based food web has been of major importance to the estuary since the clam's invasion in 1986 (Nichols et al., 1990). Fish and bird species that consume *C. amurensis* are shown (**Figure 11**). A Dungeness crab food web also is shown because the diet of the crab includes *C. amurensis*. However, little Se-specific information is known for this crab. The bald eagle food web shows the complexity of a high order trophic level predator. USFWS suggested that the bald eagle would be representative of a resident high order predator for the purposes of modeling (USFWS, 2008). Chinook salmon and steelhead, along with the California black rail, are modeled for landward sites. Invertebrate prey items, in addition to aquatic insects, that may be of importance at landward sites also are listed. Environmental partitioning factors ( $K_{ds}$ ) and Trophic Transfer Factors (TTFs) used to quantify the biotransfer of Se through food webs of the estuary also are shown in **Figure 11**. The development of these factors is shown in detail later (see *Derivation of Site-Specific Model Components* section).

A diagram across flow seasons illustrates exposure media (water, suspended particulate material, and clams) and the potential for exposure based on the life cycles and habitat-use of predators in the estuary (**Figure 12**). Migratory and resident bird and fish species are illustrated. Knowing the details of a predator's location during critical life stages for Se effects allows correlating trends in diet and exposure that occur in the estuary. This knowledge, in turn, sets choices in modeling scenarios. Combining food web, life cycle, habitat use, and effects data (**Figures 10, 11, and 12**) results in Bay-Delta specific information for criteria development.

The probable critical life stages of predators most at risk for Se effects as given in USFWS (2008) are:

- bald eagle and California clapper rail: adult female (egg laying);
- scoter and scaup: adult male and female (migration);
- Chinook salmon and steelhead: migrating/rearing juvenile; and
- green and white sturgeon and Sacramento splittail: juvenile or adult female.

The estimated maximum percentage of diet that is clam-based for each predator most at risk (USFWS, 2008) (**Figure 11**) is:

- lesser scaup 96%;
- surf scoter 86%;
- greater scaup 81%;
- black scoter 80%;
- white-winged scoter 75%;
- California clapper rail 64%;
- white sturgeon and assumed for green sturgeon 41%;
- Sacramento splittail 34%; and

- bald eagle 23%.

Specifically, migratory bird species such as surf scoter and greater and lesser scaup are at risk based on their consumption of a clam-based diet (75-96%) (**Figure 11**). Overwintering populations of diving ducks in the estuary can reach 50-92% of migrating populations (Wainwright-De La Cruz et al., 2008; Poulton et al., 2002) (**Figure 11**). Diving ducks arrive in the estuary when Se concentrations are elevated (**Figure 11**). The ducks eat voraciously as they stage for migration in the spring, which puts them at risk from chronic effects that influence many facets of their migratory and breeding behavior (**Figures 7 and 10**). Surf scoters during overwintering move throughout the North Bay and thus can be exposed to different clam species (i.e., *V. philippinarum* in the Central Bay) (Wainwright-De La Cruz, 2008). Food webs for clapper rails with an estimated 64% clam-based diet present opportunities for modeling of reproductive effects for resident species (**Figures 4 and 5**).

White and green sturgeon consume a diet that is approximately 41% clams (USFWS, 2008). Green sturgeon is a federally listed endangered species that spends more time migrating than white sturgeon. Although white sturgeon migrate upstream to spawn, they are described as semi-anadromous because they spend a substantial amount of their life in the estuary. White and green sturgeon are very long-lived (50-100 years) and have a two year internal egg maturation that is conducive to Se loading of eggs (**Figure 12**) (Linville, 2006).

Sacramento splittail is a federally listed species of concern that consumes a diet of approximately 34% clams (USFWS, 2008). This species spawns both in the upper Delta and the estuary and is known to inhabit Suisun Bay.

The USFWS (2008) stated that although the diets of salmon and steelhead trout are not known to be clam-based, these species may still be at risk from Se because of their greater toxicological sensitivity to Se. Migratory salmon and trout are known to be in the Delta during migration upstream and emigration to the ocean (**Figure 12**). Steelhead trout may be best described as nearly year-around spawners (i.e., juveniles may hold over for many months to a year and may not even emigrate to the ocean at all) (USFWS, 2008). Population numbers for the Delta smelt are alarmingly low, and thus the USFWS concluded that this species is particularly vulnerable to any adverse effect.

The giant garter snake is a federally listed species that is known to inhabit the Delta (USFWS and NMFS, 1998; amended 2000; USFWS, 2006; 2009a). The species is an aquatic predator that feeds on small fish and larval/sub-adult frogs. Modeling for this species of reptile is not included here, but future modeling could include a food web specific to the giant garter snake.

## Ecosystem-Scale Model Components

### Partitioning and Transformation

Profiles of dissolved and suspended particulate material Se concentrations across the Bay-Delta (Cutter and Cutter, 2004, Doblin et al., 2006; Lucas and Stewart, 2007) initiate ecosystem-scale modeling by developing a detailed understanding of the relationship of dissolved and particulate Se concentrations at specific landward and seaward locations (**Figure 2**). Consideration of the transformations of dissolved Se phases to particulate Se phases is critical to quantifying the entrance of Se into food webs (**Figure 13**). The environmental partitioning factor  $K_d$  is used here to operationally characterize the bioconcentration of dissolved Se into the base of the food web (**Figures 7 and 13**).  $K_d$  is environment specific and is the ratio of the particulate material Se concentration to the dissolved Se concentration. The specific equation is

$$K_d = (C_{\text{particulate material, } \mu\text{g/kg dw}}) \div (C_{\text{water, } \mu\text{g/L}}) \quad (1)$$

Note that particulate Se concentrations are usually expressed as  $\mu\text{g/g dw}$ . These units must be converted to  $\mu\text{g/kg dw}$  to make the particulate concentration comparable to the water concentration.

Dissolved Se is the preferred parameter to measure and model, although total water column Se (i.e., unfiltered Se) can be specified in the derivation of  $K_d$  for modeling to accommodate using existing datasets. Measurement of a total water column Se concentration would include a fraction attributable to digested suspended material Se. Specifically for Bay-Delta profiles or transects, dissolved Se samples were collected and dissolved Se concentrations are available (Cutter and Cutter, 2004).

A particulate material Se concentration is the other component of  $K_d$  to measure and model (**Figure 13**). The base of the food web, as sampled in the environment, can include phytoplankton, periphyton, detritus, inorganic suspended material, biofilm, sediment and/or attached vascular plants (Presser and Luoma, 2010). For simplicity in our discussion here, we define this mixture of living and non-living entities as *particulate material*. Specifically for Bay-Delta profiles and transects, suspended particulate material samples were collected and suspended particulate material Se concentrations are available (Doblin et al., 2006).

As illustrated in **Figure 13**,  $K_d$  represents phase transformation in the system (i.e., the efficiency with which dissolved Se is converted to particulate material Se). Phase transformation reactions from dissolved to particulate material Se are of toxicological significance because particulate material Se is the primary form through which Se enters food webs (Luoma et al, 1992; Presser and Luoma, 2010; Stewart et al., 2010). The different biogeochemical transformation reactions result in different forms of Se in particulate material: organo-Se, elemental Se, or adsorbed Se (**Figure 13**). The resulting particulate Se speciation, in turn, affects the bioavailability of Se to invertebrates depending upon how an invertebrate “samples” the complex water/sediment/particulate *milieu* that composes its environment. Collection of a complete dataset of particulate phases and their Se concentrations and speciation can greatly aid in quantifying the biogeochemical dynamics of an estuarine system and, hence, the prediction of prey and predator Se concentrations.

Dissolved Se species that are present will influence the type of phase transformation reaction that creates particulate Se. Examples of types of reactions and the particulate species they produce (**Figure 13**) include: 1) uptake by plants and phytoplankton of selenate, selenite or dissolved organo-Se and reduction to particulate organo-Se by assimilatory reduction (e.g., Sandholm et al., 1973; Riedel et al., 1996; Wang and Dei, 1999; Fournier et al., 2006); 2) sequestration of selenate into sediments as particulate elemental Se by dissimilatory biogeochemical reduction (e.g., Oremland et al., 1989); 3) adsorption as co-precipitated selenate or selenite through reactions with particle surfaces; and 4) recycling of particulate phases back into water as detritus after organisms die and decay (e.g., Velinsky and Cutter, 1991; Reinfelder and Fisher, 1991; Zhang and Moore, 1996). Selenate is the least reactive of the three forms of Se and its uptake by plants is slow. If all other conditions are the same,  $K_d$  will increase as selenite and dissolved organo-Se concentrations increase (even if that increase is small). Experimental data support this conclusion. Calculations using data from laboratory microcosms and experimental ponds show speciation-specific  $K_d$ s of 140-493 where selenate is the dominant form; 720-2,800 when an elevated proportion of selenite exists; and 12,197-36,300 for 100% dissolved seleno-methionine uptake into algae or periphyton (Besser et al., 1989; Graham et al., 1992; Kiffney and Knight, 1990).

Measurement of suspended particulate material Se concentrations in the Bay-Delta, therefore, is important for initiating modeling, understanding the extent of biological transformations, and developing accuracy within the model. Data collection in site-specific field situations for particulate phases can include benthic or suspended phytoplankton, microbial biomass, detritus, biofilms, and nonliving organic materials associated with fine-grained ( $<100 \mu\text{m}$ ) surficial sediment (Luoma et al.,



1992). Analysis of particulate Se and particulate Se speciation of each phase collected would account for partitioning of Se in different media and elucidate how  $K_d$  may be best defined to represent the dynamic conditions present in the estuary. If few data are available to characterize particulate phases or data are inconsistent as to a particle type that can be compared among locations, the greater the uncertainty in any predictions. Further information on choice of particulate material type, sample collection in aquatic systems, and modeling limitations are given in Presser and Luoma (2010). For example,  $K_d$  can be influenced by the type of particulate material collected where a hierarchy of Se concentrations exist within an ecosystem (e.g., 2.4  $\mu\text{g/g}$  in sediment; 3.2  $\mu\text{g/g}$  biofilm, and 5.5  $\mu\text{g/g}$  for filamentous algae). Using these concentrations with a field-measured dissolved Se concentration would yield a range of  $K_d$ s that reflects the complexities of the system. In this regard, collection of one consistent type of material is an option, with bed sediments (especially if the sediments vary from sand to fine-grained) among the samples being the least desirable choice for calculating  $K_d$ .

### Biodynamics: Invertebrates, Fish, and Birds

Kinetic bioaccumulation models (i.e., biodynamic models, Luoma and Fisher, 1997; Luoma and Rainbow, 2005) account for the now well-established principle that Se bioaccumulates in food webs principally through dietary exposure. Tissue Se attributable to dissolved exposure makes up less than 5% of overall tissue Se in almost all circumstances (Fowler and Benayoun, 1976; Luoma et al., 1992; Roditi and Fisher, 1999; Wang and Fisher, 1999; Wang 2002; Schlekot et al., 2004; Lee et al., 2006). Biodynamic modeling (**Figures 6 and 8**) shows that the extent of Se bioaccumulation (the concentration achieved by the organism) is driven by physiological processes specific to each species (Reinfelder et al., 1998; Wang 2002; Baines et al., 2002; Stewart et al., 2004). Biodynamic models have the further advantage of providing a basis for deriving a simplified measure of the linkage between trophic levels: TTFs (**Figure 7**). For each species, a TTF can be derived from either experimental studies or field observations, where the TTF defines the relationship between Se concentrations in an animal and in its food (**Figure 7**).

Experimental derivation of TTFs is based upon the capability of a species to accumulate Se from dietary exposure as expressed in the biodynamic equation (Luoma and Rainbow, 2005):

$$dC_{\text{species}}/dt = [(AE) (IR) (C_{\text{food}})] - (k_e + k_g)(C_{\text{species}}) \quad (2)$$

where  $C$  is the contaminant concentration in the animal ( $\mu\text{g/g dw}$ ),  $t$  is the time of exposure in days ( $d$ );  $AE$  is the assimilation efficiency from ingested particles (%);  $IR$  is the ingestion rate of particles ( $\text{g/g/d}$ );  $C_{\text{food}}$  is the contaminant concentration in ingested particles ( $\mu\text{g/g dw}$ );  $k_e$  is the efflux rate constant ( $/d$ ) that describes Se excretion or loss from the animal; and  $k_g$  is the growth rate constant ( $/d$ ). The equation shows that key determinants of Se bioaccumulation are the ingestion rate of the animal, the efficiency with which Se is assimilated from food, and the rate constant describing Se turnover or loss from the tissues of the animal (Luoma and Rainbow, 2005). Experimental protocols for measuring such parameters as  $AE$ ,  $IR$ ,  $k_e$  are now well developed (Wang et al., 1996; Luoma and Rainbow, 2005).

In the absence of rapid growth, a simplified, resolved biodynamic exposure equation for calculating a Se concentration in an invertebrate is

$$C_{\text{invertebrate}} = [(AE) (IR)(C_{\text{particulate}})] \div [k_e] \quad (3)$$

where  $C_{\text{food}}$  is defined as  $C_{\text{particulate}}$ .

For modeling, these physiological parameters can be combined to calculate a  $\text{TTF}_{\text{invertebrate}}$ , which characterizes the potential for each invertebrate species to bioaccumulate Se.  $\text{TTF}_{\text{invertebrate}}$  is defined as

$$\text{TTF}_{\text{invertebrate}} = [(AE) (IR)] \div k_e \quad (4)$$

Similarly, foodweb biodynamic equations for fish and birds are

$$C_{\text{fish or bird}} = [(AE) (IR) (C_{\text{invertebrate}})] \div k_e \text{ and } \text{TTF}_{\text{fish or bird}} = [(AE) (IR)] \div k_e \quad (5) \text{ and } (6)$$

When laboratory data are not available, a field  $TTF_{invertebrate}$  can be defined from matched datasets (in dw or converted to dw) of particulate and invertebrate Se concentrations as

$$TTF_{invertebrate} = C_{invertebrate} \div C_{particulate} \quad (7)$$

A field derived species-specific  $TTF_{fish}$  is defined as

$$TTF_{fish} = C_{fish} \div C_{invertebrate} \quad (8)$$

where  $C_{invertebrate}$  is for a known prey species,  $C_{fish}$  is reported as muscle or whole-body tissue, and both Se concentrations are reported in  $\mu\text{g/g dw}$ . If necessary, the modeling approach can represent a diet that includes a mixed proportion of prey in the diet through use of the equation

$$C_{fish} = (TTF_{fish}) [(C_{invertebrate a}) (\text{prey fraction}) + (C_{invertebrate b}) (\text{prey fraction}) + (C_{invertebrate c}) (\text{prey fraction})] \quad (9)$$

Once TTFs are known, invertebrate Se concentrations are calculated from particulate material Se concentrations through use of the equation

$$C_{invertebrate} = (TTF_{invertebrate}) (C_{particulate}) \quad (10)$$

Equations are combined to represent step-wise bioaccumulation from particulate material through invertebrate to fish as

$$C_{fish} = (TTF_{invertebrate}) (C_{particulate}) (TTF_{fish}) \quad (11)$$

Similarly for birds, the combined equation is

$$C_{bird} = (TTF_{invertebrate}) (C_{particulate}) (TTF_{bird}) \quad (12)$$

Modeling can accommodate longer food webs that contain more than one higher trophic level consumer (e.g., forage fish being eaten by predatory fish) by incorporating additional TTFs. One equation for this type of example is

$$C_{predator fish} = (TTF_{invertebrate}) (C_{particulate}) (TTF_{forage fish}) (TTF_{predator fish}) \quad (13)$$

Modeling for bird tissue also can represent Se transfer through longer or more complex food webs (e.g., TTFs for invertebrate to fish and fish to birds) as

$$C_{bird} = (TTF_{invertebrate}) (C_{particulate}) (TTF_{fish}) (TTF_{bird}) \quad (14)$$

Variability or uncertainty in processes that determine AEs or IRs can be directly accounted for in sensitivity analysis (Wang et al, 1996). That is accomplished by considering the range in the experimental observations for the specific animal in the model. Field derived factors require some knowledge of feeding habits and depend upon available data for that species. Laboratory and field factors for a species can be compared and refined to improve levels of certainty in modeling. Hence, physiological TTFs derived from kinetic experiments for a species and ecological TTFs derived either from data for a species across different field sites (global) or from one site (site-specific) are of value in modeling and understanding an ecosystem.

TTFs are species-specific because of the influence of the physiology of the animal. They may vary to some extent as a function of the concentration in food or if AE or IR vary (Besser et al., 1993; Luoma and Rainbow, 2005). The approach here leads to consideration of a single TTF to quantify trophic transfer from diet to tissue for each species illustrated in modeling. If enough data are available to develop diet-tissue concentration regressions specific to inhabitants of an estuary or watershed, then use of those regressions would provide more detailed relationships than single determinations. Additionally, in nature, if it is assumed that organisms regulate a constant minimum concentration of Se, then the observed TTF will increase when the concentration in food is insufficient to maintain the regulated concentration (Beckon et al., 2008). Datasets from which non-site-specific TTFs were derived for use in modeling here were collected from sites exposed to Se contamination and identified as problematic because of Se bioaccumulation (Presser and Luoma, 2010). However, discretion was used when considering datasets from extremely contaminated sites (e.g., Kesterson). The relatively small

variation of TTF within taxonomically similar animals is evidence that these potential sources of uncertainty may be minimal in terms of biodynamic kinetics variations (Presser and Luoma, 2010).

## Available Data

**Table 7** lists available data for the Bay-Delta. Comprehensive data collection to evaluate Se concentrations in the Bay-Delta began in 1986. Transects of the Bay-Delta from November 1997 to November 1999 provide spatially and temporally matched datasets for samples collected at one meter below the surface (Cutter and Cutter, 2004; Doblin et al., 2006). The parameters measured for these datasets were:

- salinity;
- dissolved Se concentration;
- dissolved Se speciation;
- suspended particulate material Se concentration;
- suspended particulate material Se speciation;
- amount of total suspended material; and
- particulate carbon (C) concentration.

Transects during July, 2000 to January, 2004 characterize the area mainly from Rio Vista and Stockton to Benicia near the Carquinez Strait (Lucas and Stewart, 2007) (**Figure 1**). These more landward transects were limited to:

- dissolved Se;
- dissolved Se speciation; and
- suspended particulate material Se concentration.

Not all datasets are complete, so graphed profiles shown later may vary somewhat because matched pairs for each combination of data (e.g., dissolved Se and suspended particulate material Se in comparison to percentage of suspended particulate organo-Se) across the salinity gradient were not always available.

The matched data pairs for dissolved Se concentrations and suspended particulate material Se concentrations used here are for tidally-influenced sites. Doblin et al. (2006) hydrodynamically categorized (i.e., binned), for the conditions of each transect, the most landward suspended particulate material Se samples as *the Delta*. These Delta sites are nominally upstream of Chippis Island (Doblin et al., 2006) and, thus, these sites are tidally influenced (**Figure 1**). Therefore, our site-specific derivation does not address Se concentrations in end-members such as the Sacramento and San Joaquin Rivers (i.e., Sacramento River at Freeport and the San Joaquin River at Vernalis).

The methodology for collection and analysis of dissolved and suspended particulate material Se samples is described in Doblin et al. (2006). Methods for determining particulate Se can result in presentation of data either as  $\mu\text{g/L}$  or  $\mu\text{g/g}$ . For work here, direct determination of particulate Se concentrations as  $\mu\text{g/g dw}$  is preferable. However, a particulate Se concentration in  $\mu\text{g/L}$  can be converted to  $\mu\text{g/g dw}$  through division by the available matched data on amount of total suspended material (in  $\text{mg/L}$ ). Because of the limited data available for characterization of the Bay-Delta and the data needs of modeling for criteria development, all necessary conversions were made in order to make full use of available data. Future monitoring of the Bay-Delta should consider collection of suspended particulate material Se concentration data as  $\mu\text{g/g dw}$ . All solids are expressed in dry weight (dw).

Other types of datasets are available for the Bay-Delta (**Table 7**). Meseck (2002) collected sedimentary Se samples from box-cores and extracted pore waters from Bay-Delta locations from 1997-1999. Sedimentary Se samples (sediment cores at 2-4 meter-depth of water) also were collected in 1998

from six locations in the Delta (M. Doblin, personal communication March, 2009) and in 2000 from three locations in the Delta (Lucas and Stewart, 2007) (**Table 7**).

Datasets for Se concentrations in specific predators and food webs (e.g., the clam, *C. amurensis*, white sturgeon, surf scoter) also are listed (**Table 7**), but few current, matched datasets are available to provide comprehensive documentation of food webs. Fifteen years of monitoring data in the northern estuary for Se in *C. amurensis* was recently published (Kleckner et al., 2010) and is illustrated later in the report. **Appendix D (Tables D1-D5)** gives a compilation of some of the available food web Se data including for invertebrates, fish, and birds. Because there are minimal data available, data are generalized in model validations; however, data used in validation scenarios and illustrations are as closely matched as possible.

## Application of Ecosystem-Scale Methodology

### Estuarine Approaches

A methodology based on a salinity gradient across the Bay-Delta, from the tidally-influenced landward sites above Chipps Island to seaward sites near the Pacific Ocean at the Golden Gate Bridge (Cutter and Cutter, 2004; Doblin et al., 2006; Lucas and Stewart, 2007) is used here to provide location-specific modeling for the estuary (Presser and Luoma, 2006). Given a specific food web and Se tissue guideline, the approach uses salinity-specific data to derive  $K_d$ s and TTFs and to predict allowable dissolved Se concentrations at each salinity measured across an estuary profile. This gradient modeling approach illustrates the variability across the estuary in terms of transformations, bioaccumulative potential, and protective dissolved allowable Se concentrations (**Figures 2 and 9**). A generalized approach (i.e., using a mean  $K_d$  from a transect) would add uncertainty to the derivations and predictions because of, for example, inclusion of samples from freshwater and ocean interfaces. Mean Se concentrations for transects can be used as a way to compare datasets through time, but that approach may be of limited applicability. Other statistical parameters or analysis techniques also could be used (i.e., median, 75<sup>th</sup> percentile value) for comparison of estuarine conditions.

A second modeling approach, a focused location approach, uses compartmentalized data for Suisun Bay and Carquinez Strait (Doblin et al., 2006) to illustrate how the Bay-Delta can be divided into segments for explicit regulatory consideration (**Figure 14**). Doblin et al. (2006) grouped particulate material Se samples as a function of salinity into four embayments: 1) Central Bay; 2) San Pablo Bay; 3) Carquinez Strait-Suisun Bay; and 4) Delta. **Figure 14** shows the range of suspended particulate material Se concentrations within the compartmentalized segments and the patterns within the range of illustrated flow conditions. Focusing on transect samples that specifically represent Carquinez Strait-Suisun Bay allows modeling and prediction for the localized area most affected by internal oil refinery Se sources and for time periods of specified flow conditions. Again, a mean or other statistical measure for each transect, but within the Suisun Bay-Carquinez Strait segment, can be used to characterize conditions through time, but thus at a more narrowly defined site.

Modeling that specifies 1) water-year type and flow season; or 2) freshwater residence time further narrows uncertainties within the estuarine approaches by addition of a temporal component. Modeling of the Bay-Delta based on hydrologic season or residence time also enables connection to hydrodynamic cycles, prey/predator exposure, and habitat-use (**Figure 12**) in developing site-specific allowable Se concentrations. Specific dates, freshwater residence times, water-year types, and flow seasons for transects of the Bay-Delta (Cutter and Cutter, 2004; Doblin et al., 2006) are:

- November 5-6, 1997, 68 days, wet year, low flow season;
- June 16-17, 1998, 11 days, wet year (El Niño), high flow season;

- October 7-8, 1998, 22 days, wet year, low flow season;
- April 13-14, 1999, 16 days, wet year, and high flow season; and
- November 4-5, 1999, 70 days, above normal year, low flow season.

The conditions in the estuary during these transects and the proportion of the recent historical record represented by these five transects are given context by showing the sampling dates within the variability afforded by NDOI for the period 1996-2009 (**Figure 15**). During an 11-day residence time in June, 1998, NDOI is 73,732 cfs as a daily average/month, but during a 70-day residence time in November, 1999, NDOI is 6,951 cfs as a daily average/month. Thus, consideration of a temporal component in modeling may be imperative for applying predictions here to conditions in the estuary in the future.

## Dissolved and Suspended Particulate Material Selenium Profiles for Modeling

Modeling and predictions for criteria development for a *C. amurensis* food web uses Se data from the Bay-Delta transects listed above (November, 1997; June and October, 1998; April and November, 1999) (**Figures 16 and 17**). Transect sampling for the Bay-Delta included 19 to 20 sites per transect, except for the June 1998 transect, which included 13 sites. Conditions represented are all wet or above normal years, with sampling in June, 1998 and April, 1999 being during high flow seasons and October, 1998, November, 1997, and November, 1999 being during low flow seasons (**Figure 15**).

Salinity at the Golden Gate Bridge varies from 24.8 to 32.5 psu for the five transects. Distinctive profiles for dissolved Se concentrations from June 1998 shows conditions in the Bay-Delta when flows were exceptionally high because of extremely wet conditions related to El Niño (**Figures 16**). Approximately 70% of the data for this transect was obtained at sites with salinities < 5 psu. In contrast, profiles for residence times of 68 to 70 days in November, 1997 and 1999 show a span of salinities up to approximately 32 psu.

Specifically, **Figure 16** shows dissolved Se concentrations across the estuary during a progression of residence times (11-70 days) from November, 1997 to November, 1999. The transect for November, 1997 is separated out from the main analysis here because of 1) decreasing refinery Se loads as proposed reductions took place (**Table 1; Figure 3**); and 2) a noticeably higher dissolved Se concentration-profile across the estuary. The range of dissolved Se concentrations is narrowly defined as 0.070-0.320  $\mu\text{g/L}$  for all Bay-Delta transects (**Table 8**).

The range of suspended particulate Se concentrations (0.15-2.2  $\mu\text{g/g dw}$ ) for all Bay-Delta transects is not as narrowly defined as that for dissolved Se (**Figure 17; Table 8**). The patterns of particulate enrichment vary with specified flow condition (e.g., April, 1999; November, 1999). The variation at freshwater and ocean interfaces would contribute differently (or may contribute substantially) to a calculated overall mean condition. Also depicted is the variation in calculated  $K_{dS}$  across the estuary. These  $K_{dS}$  will be used later as critical location-specific inputs for ecosystem modeling.

A subset of dissolved and suspended particulate material Se concentrations is developed using the samples defined as Suisun Bay-Carquinez Strait in **Figure 14** (Cutter and Cutter, 2004; Doblin et al., 2006) (**Table 9**). The range of dissolved Se concentrations is from 0.076-0.215  $\mu\text{g/L}$  and the range of suspended particulate material Se concentrations is 0.15-1.0  $\mu\text{g/g dw}$ .

Profiles of dissolved and suspended particulate Se concentrations also are derived from more limited transects of the estuary from Rio Vista and Stockton to Benicia during 2003 and 2004 (**Figure 18**). Four transects (January, April, and October, 2003; January, 2004) are used to model an aquatic insect food web. Specific dates, water-year types, and flow seasons for transects (Lucas and Stewart, 2007) are:

- January 22, 2003, above normal year, high flow season;
- April 22-23, 2003, above normal year, high flow season;
- October 10, 2003, below normal year, low flow season; and
- January 15, 2004 below normal year, high flow season.

As previously noted, samples for these transects were taken as part of work defining processes in the Delta (Lucas and Stewart, 2007), but sampling was extended to some seaward locations in the estuary (i.e., near Benicia). NDOI (daily average per month) varies from 4,350 to 50,847 cfs over the range of transects, with October, 2003 representing a below normal year-low flow condition. The range of dissolved Se concentrations is 0.068-1.01  $\mu\text{g/L}$  and the range of suspended particulate material Se concentrations is 0.23-1.5  $\mu\text{g/g dw}$  (**Table 10**).

## Dissolved and Suspended Particulate Material Selenium Speciation

Selenium speciation in source discharges and within the gradient of the estuary itself are important in quantifying the efficiency of transformations from dissolved Se to particulate Se (**Figure 2**). Profiles of dissolved Se speciation across the salinity gradient for September, 1986 and November, 1997 show that the percentages of dissolved selenite generally have decreased over time (Cutter, 1989; Cutter and Cutter, 2004) (**Figure 19**). During the period 1992-1998, new treatment technologies were put into place that were designed to reduce the amount of dissolved selenite in the effluent (San Francisco Bay Board, 1992a,b; 1993). Other factors to consider in broad comparisons such as these, are that the salinity for Carquinez Strait near the refineries during November, 1997 ranged from approximately 12 to 19 psu (Doblin et al., 2006) and that the residence time was 24 days during the 1986 transect and 70 days during the 1997 transect.

**Figure 20** shows profiles across the Bay-Delta of suspended particulate material organo-Se concentrations as the percentage of the total of the three suspended particulate material Se species analyzed [(i.e., organo-Se, elemental Se, and inorganic Se (adsorbed selenate and selenite), Doblin et al., 2006]. The patterns of organo-Se particulate enrichment identified here serve as the basis for quantifying the effects of transformations to particulate material Se (i.e.,  $K_d$ ) and the assimilation efficiency of Se in the particulate material by prey (i.e., understanding the particulate material to prey kinetics of bioaccumulation).

## Bioaccumulated Selenium in Prey

Central to the seaward ecosystem is the *C. amurensis* food web (Nichols et al., 1990; Linville et al., 2002; Presser and Luoma, 2006). **Figure 21** shows monthly mean Se concentrations for *C. amurensis* from several USGS monitoring stations for the time periods encompassed by the Bay-Delta transects (see inset). Mean observed *C. amurensis* Se (Kleckner et al., 2010) for each transect (Cutter and Cutter, 2004; Doblin et al., 2006) are shown in order of high flow seasons (June, 5.4  $\mu\text{g/g dw}$  and April, 7.3  $\mu\text{g/g dw}$ ) to low flow seasons (October, 10.8  $\mu\text{g/g dw}$  and November, 11.3; 14.3  $\mu\text{g/g dw}$ ) during wet or above normal years (**Figure 21**) (see additional discussion in *Choices, Limitations, and Reduction of Uncertainty* section). Data here illustrate the connection of bivalve Se concentrations to the cumulative productivity of the estuary in terms of Se transformation, uptake, and exposure during low flow periods. The variability within the available 15-year monthly *C. amurensis* Se concentration dataset is illustrated to give context to means for 1997-1999 (grand mean, 12.1  $\mu\text{g/g dw}$ ).

Less data are available for landward insect-based food webs (**Table 7; Appendix D, Table D5**). Data for invertebrate Se concentrations are from 2001 and 2002, with means ranging from 0.6-4.8  $\mu\text{g/g}$

dw. With limited invertebrate data, patterns and connections to hydrodynamic and ecological cycles are difficult to assess.

## Derivation of Site-Specific Model Components

### Environmental Partitioning Factors ( $K_{ds}$ )

Location-specific  $K_{ds}$  based on salinity across the Bay-Delta are calculated from spatially and temporally matched datasets for dissolved and suspended particulate material Se (**Figures 17 and 18; Tables 8, 9, and 10**). Statistical evaluations of dissolved and suspended particulate material Se concentrations for complete transects or focused Suisun Bay-Carquinez Strait transect yield a set of mean, 75<sup>th</sup> percentile, median, and 25<sup>th</sup> percentile  $K_{ds}$  (**Tables 11 and 12**). The location-specific  $K_{ds}$  and set of statistical  $K_{ds}$  are then used to represent conditions in the estuary for modeling a seaward clam-based food web and predicting an allowable dissolved Se concentration. The set of  $K_{ds}$  used to represent conditions in the estuary for modeling a landward insect-based food web and predicting an allowable dissolved Se concentration is shown in **Table 10**.

Location-specific  $K_{ds}$  show the variation that can be expected across the estuary in the recent past (**Figures 17 and 18**).  $K_{ds}$  vary similarly as suspended particulate material Se concentrations do across transects because of the narrowly defined range of dissolved Se concentration. For Bay-Delta transects,  $K_{ds}$  range from 712 to 26,912 (**Figure 17; Table 8**). For Suisun Bay-Carquinez Strait transects,  $K_{ds}$  range from 712 to 7,725 (**Table 9**). For Rio Vista and Stockton to Benicia transects,  $K_{ds}$  range from 554 to 12,650 (**Table 10**). As noted previously, these latter transects also extend to seaward locations and, hence, calculated means include combinations of data from both landward and seaward locations. These means and ranges for  $K_{ds}$  agree well with compiled field datasets for  $K_{ds}$  for estuaries and choices used in previous Bay-Delta modeling scenarios (i.e., 3,000 to 10,000) (Presser and Luoma, 2006; Presser and Luoma, 2009; Presser and Luoma, 2010).

### Trophic Transfer Factors (TTFs)

#### Clam (*C. amurensis*)

The choice of food web is critical to modeling success because the particulate material to prey kinetics of bioaccumulation differs widely among invertebrates (Presser and Luoma, 2010).  $TTF_{C. amurensis}$  derived from laboratory experiments averaged 6.25 over a range of assimilation efficiencies, ingestion rates, and efflux rate constants (Presser and Luoma, 2010). This average is within a range of 0.6 to 23 for invertebrate species, with TTFs for species of bivalves being the highest (Presser and Luoma, 2010).

Experimental physiological biodynamic parameters and rates are derived under idealized conditions in the laboratory. These biodynamic equations can be adjusted for a specific ecosystem by incorporating data from that system (Presser and Luoma, 2010).  $TTF_{C. amurensis}$  is developed here for the estuary from a mechanistic equation for quantifying the biodynamics of *C. amurensis* and estuary-specific data for suspended particulate material (i.e., the food for clams). Selenium bioaccumulated at steady state by *C. amurensis* is calculated using a site-specific modification of equation (3)

$$C_{C. amurensis} = [(AE) (IR) (C_{\text{suspended particulate material}}) \div (k_e)] \quad (14)$$

where  $(AE) (IR)/k_e$  is defined as  $TTF_{C. amurensis}$  and  $C_{\text{food}}$  is defined as the Se concentration in estuary suspended particulate material ( $C_{\text{suspended particulate material}}$ ). Among field data available to quantify site-specific biodynamics of *C. amurensis* are spatially and temporally matched datasets from estuary transects (Doblin et al., 2006) for:

- suspended particulate material Se concentration;
- suspended particulate material C concentration;
- percentage of C in suspended particulate material; and
- percentages of suspended particulate elemental Se, adsorbed Se, and organo-Se.

Our site-specific approach here differs from broader approaches where 1) laboratory data for biodynamic parameters such as AE and IR of particulate material may be generalized; 2) particulate Se concentrations may be an average of several phases of material (i.e., particulate Se<sub>total</sub>); or 3) field data may be sparse and thus applied across an entire watershed (Presser and Luoma, 2009).

In general, for the purposes of a Bay-Delta location and estuarine processes, the suspended particulate material Se concentration carries with it assumptions about Se being associated primarily with organic material (detritus and living organisms). This allows us to determine IR on the same organic material basis (assuming clams seek organic material in the suspended particulate material) and to refine AE to account for suspended particulate material speciation (i.e., divide AE into three components of Se in suspended particulate material and their individual bioavailabilities). These assumptions are all rooted in well established biological understanding of bivalve feeding (Cammen, 1980; Lopez and Levinton, 1987). We ignore the possibility of uptake directly from water by the clams because that has been shown in a large body of work to be trivial (Luoma and Rainbow, 2005).

Justifications for values used in each parameter of the equation for a site-specific approach are:

1. We can either assume that Se is associated with carbonaceous materials or Se is spread across all suspended particulate material. For the former, the concentration of Se is expressed as  $\mu\text{g Se/g C}$ . We obtain  $\mu\text{g Se/g C}$  by dividing the suspended particulate material Se concentration ( $\mu\text{g Se/g suspended particulate material}$ ) by  $\text{mg C/mg suspended particulate material}$ . For the present calculations we employ suspended particulate material Se concentrations as justified below.
2. IR is determined by filtration rate (125 L/g clam/d, Cole et al., 1992) multiplied by C (median = 0.4 mg C/L) to achieve the units (g C/g clam/d) in the suspended particulate material at each sampling. In the average condition in the estuary, clams ingest 5% of their body weight per day in C across all days for which data is available. At an average of 2% C in suspended particulate material (again, the average across all data) they ingest 2.5 times their body weight per day in total suspended particulate material. If IR is calculated at each of three low river discharge months where data is available, the average is 1.7 g suspended particulate material/g clam/d. Experience has indicated that the ingestion model is more accurate when actual outcomes are used (or averaged) for the generic situation (i.e., 1.7 g suspended particulate material/g clam/d) as compared to taking the average of each component of the outcome and calculating a generic average. Therefore, we recommend using 1.7 g suspended particulate material/g clam/d for modeling.
3. The derivation of a refined site-specific AE based on individualized bioavailabilities of Se in suspended particulate material uses observed fractions of particulate organo-Se, adsorbed Se, or elemental Se found in the estuary (Doblin et al., 2006) combined with individual AEs for those particulate Se species from the literature (living phytoplankton, AE = 60%; adsorbed on seston, AE = 40%; elemental, AE = 0%; Schlekot et al., 2004; Wang et al., 1996). The equation is:
 
$$\text{AE} = (\text{fraction organic particulate Se}) (\text{AE}_{\text{organic particulate Se}}) + (\text{fraction adsorbed particulate Se}) (\text{AE}_{\text{adsorbed particulate Se}}) + (\text{fraction elemental particulate Se}) (\text{AE}_{\text{elemental particulate Se}}) \quad (15)$$

For example, if a site-specific sample of suspended particulate material collected in the estuary contains 45% Se in phytoplankton at an assumed AE of 60%; 30% Se adsorbed on seston at an



assumed AE of 40%; and 25% elemental Se in sediment at an assumed AE of 0%, then the composite AE = (0.45 x 0.6) + (0.30 x 0.40) + (0.25 x 0) = 0.39 or 39% AE.

4. We apply the efflux rate constant derived experimentally (Lee et al., 2006):  $k_e = 0.03/\text{d}$ .
5. When we model for times when all data are available from the estuary, we use all data from that sampling date. When we model generically we employ mean parameters.

Given the above protocol and assumptions, we can directly calculate *C. amurensis* Se concentrations for comparison to observed Se concentrations to validate predictions or calculate a  $\text{TTF}_{C. amurensis}$  for use in modeling. If the data and assumptions given above are used in a site-specific modification of equation (4)

$$(\text{IR}) (\text{AE}) \div k_e = \text{TTF}_{\text{clam}} \quad (16)$$

then

$$\text{TTF}_{\text{clam}} = (1.7 \text{ g suspended particulate material/g clam/d}) (0.39) \div 0.03 = 22.1$$

Or, in terms of a *C. amurensis* Se concentration, if a 0.84  $\mu\text{g/g dw}$  suspended particulate material Se concentration is assumed, then

$$C_{C. amurensis} = (0.84 \mu\text{g Se/g}) (1.7 \text{ g/g/d}) (0.39) \div 0.03/\text{d} = 18.6 \mu\text{g Se/g}$$

Salinity-specific or transect specific Se concentrations and TTFs for *C. amurensis* can be calculated using the same protocol as above, but with percentages of C and suspended particulate material Se species observed in that transect. Thus, an individual *C. amurensis* Se concentration and  $\text{TTF}_{C. amurensis}$  can be calculated from each matched set of data from the five suspended particulate material transects for the estuary (Doblin et al., 2006), making the predictions and derivations as detailed as the data permit. This data-intensive approach yields a mean  $\text{TTF}_{C. amurensis}$  of 17.1 excluding April, 1999 transects data as out of the norm (i.e., El Niño condition in the estuary) or 18.1 using the focused approach for Suisun Bay-Carquinez Strait. We assume a  $\text{TTF}_{C. amurensis}$  of 17 in modeling scenarios here. The range of TTFs across all estuarine conditions was 14-26. These values are higher than laboratory-derived values primarily because ingestion rates are higher in these field systems than in experiments. This is the first calculation of a field-derived TTF for a marine bivalve species.

### Aquatic Insect and Other Invertebrates

A Se  $\text{TTF}_{\text{insect}}$  of 2.8 is used here for modeling a landward aquatic insect food web based on a compilation of insect TTFs by Presser and Luoma (2010) (**Figure 11**). This value represents a mean TTF derived from matched field datasets for particulate Se and insect Se concentrations in freshwater environments for several species of aquatic insects including mayfly, caddisfly, dragonfly, midge and waterboatman. TTFs for other potential invertebrates in landward food webs (range is 0.6 to 2.8) are shown in **Figure 11** (Presser and Luoma, 2010).

### Bird Egg

Selenium TTFs for aquatic bird eggs are derived from data listed in USFWS (2009b) that is compiled from Heinz et al. (1989). TTFs calculated from matched data pairs for diet and bird egg tissue show a range of  $\text{TTF}_{\text{bird egg}}$  from 0.87 to 4.7. The mean  $\text{TTF}_{\text{bird egg}}$  is 2.7. If dietary Se concentrations that are unrealistic for estuary food webs are eliminated ( $< 1 \mu\text{g/g dw}$  and  $> 18 \mu\text{g/g dw}$ ), then a similar mean for  $\text{TTF}_{\text{bird egg}}$  or 2.6 is calculated. A  $\text{TTF}_{\text{bird egg}}$  of 2.6 is used here for modeling (**Figure 11**). A regression equation for diet and egg Se concentrations could be used in future modeling if scenario choices are specific enough in terms of dietary Se concentrations for birds and enough laboratory or field data are available. Modeling by Presser and Luoma (2010) showed a similar range for  $\text{TTF}_{\text{bird egg}}$ , but a somewhat lower TTF of 1.8 was chosen for modeling, which was near the lower limit for the captive mallard studies.

## Fish Whole-Body or Muscle

A Se  $TTF_{\text{fish}}$  of 1.1 is used here for modeling based on a compilation of fish TTFs by Presser Luoma (2010) (**Figure 11**). This value represents a mean TTF derived from laboratory experiments and from matched field datasets for invertebrate and fish Se concentrations in saltwaters and freshwater environments (Presser and Luoma, 2010). TTFs derived from laboratory data from biodynamic experiments range from 0.51- 1.8. TTFs for different fish species derived from field studies range from 0.6 to 1.7. TTFs derived specifically for white sturgeon range from 0.6 to 1.7, with a mean of 1.3. Selenium TTFs for fish also can be derived from data given in USFWS (2009b) (**Table 5**). If data provided for laboratory dietary Se concentrations are limited to a range of 1 to 20  $\mu\text{g/g dw}$  and the corresponding fish tissue Se concentrations, then TTFs calculated from the USFWS data range from 0.32 to 5.6, with a mean of 1.07. Again, as for modeling for birds, a regression equation for diet and fish whole-body or muscle Se concentrations could be used in future modeling if scenario choices are specific enough in terms of dietary Se concentrations for fish and enough laboratory or field data are available.

## Validation

### Prediction of Selenium Concentrations in *C. amurensis*

In general, biodynamic modeling is validated for a site location or food web by comparing predicted Se concentrations to observed Se concentrations. Monthly mean observed clam Se concentrations from USGS monitoring station 8.1 near Carquinez Strait from 1996-2009 (Linville et al., 2002; Kleckner et al., 2010) show the range of Se concentrations in *C. amurensis* (**Figure 21**). **Figure 21** also shows the time period (see inset) and compiled observed Se concentrations for *C. amurensis* from all monitoring stations during the transect collection period from November, 1997 to November, 1999. Each transect time period was two days, but reported clam data are several monthly averages near the transect collection.

Observed *C. amurensis* Se concentrations compare well with predicted Se concentrations using the biodynamic methodology described above (**Table 13**). Specific illustrated examples from the November, 1999 and June, 1998 estuary transects predict the variability seen in clams during the low flow season with a residence time of 70 days (12.6  $\mu\text{g/g dw}$  observed versus 14.1  $\mu\text{g/g dw}$  predicted) and a high flow season with a residence time of 11 days (4.4  $\mu\text{g/g dw}$  observed versus 6.6  $\mu\text{g/g dw}$  predicted), respectively (**Figure 22**).

### Prediction of Existing Conditions Across Media

Comprehensive validation of Bay-Delta ecosystem-scale modeling (**Figure 9**) is through prediction of Se concentrations in water, suspended particulate material, and tissues of food-web species during times when observed datasets are available. The generalized equation for translation of a fish tissue Se concentration to dissolved or water-column Se concentration is shown in **Table 2** and **Figure 7**. Simulations here include conditions for 1) the estuary during November, 1999 for a clam-based food web (**Table 14**); 2) Suisun Bay-Carquinez Strait during November, 1999 for a clam-based food web (**Table 15**); and 3) the estuary during 2003-2004 for a landward insect-based food web (**Tables 16**). Datasets are matched as much as possible given the scarcity of available data across all media. Several choices for  $TTF_{\text{sturgeon}}$ ,  $TTF_{C. amurensis}$ , and  $K_d$  that are based on the ranges derived for the estuary are illustrated.

Using existing Se concentrations in seaward white sturgeon, landward white sturgeon, and largemouth bass in the Delta (Stewart et al., 2004; Foe, 2010) as the starting points for modeling, predicted prey, suspended particulate material, and dissolved Se concentrations are comparable to the range of observed conditions and most are within the range of observed Se concentrations (**Tables 14-16**). Simulations across the gradient of the Bay-Delta for a clam-based food web are calculated using both a seaward and a landward observed sturgeon Se concentration to test the uncertainty within a continuum approach (**Table 14**). The more focused Suisun Bay-Carquinez Strait simulations better narrow the range of suspended particulate material Se concentrations (**Table 15**). Simulations for an insect-based food web are all within observed dissolved Se concentrations (**Table 16**).

## Modeling Scenarios and Predictions

### Bay-Delta Continuum

Site-specific model parameters and methodology steps are illustrated in **Figure 9**; exemplified food webs are shown in **Figure 11**; and life cycles for critical phases and habitat are shown in **Figure 12**. Tissue Se concentrations and specified EC levels used as regulatory guidelines are from **Tables 5 and 6**. Species, modeled tissue guidelines, and associated ECs include:

- adult female white sturgeon (whole-body) at EC10 and 05 (8.1 and 7.0  $\mu\text{g/g dw}$ );
- generic fish (whole-body) (5.0  $\mu\text{g/g dw}$ );
- juvenile white sturgeon (diet) EC10 and 05 (1.6 and 0.95  $\mu\text{g/g dw}$ );
- scoter or scaup (egg) at EC10, 05, and 0 (7.7, 5.9, 2.8  $\mu\text{g/g dw}$ );
- scoter or scaup (diet) at EC10, 05, and 0 (5.3, 4.4, 2.3  $\mu\text{g/g dw}$ );
- generic bird (egg) (same as above for EC10 egg of 7.7  $\mu\text{g/g dw}$ );
- juvenile salmon (whole-body) at EC10, 05 and 0 (1.8, 1.5, 1.0  $\mu\text{g/g dw}$ ); and
- juvenile salmon (diet) at EC10, 05, and 0 (2.7, 2.2, 1.5  $\mu\text{g/g dw}$ ).

Targets for trout inhabiting the Delta are encompassed within those for salmon with the exception of extremely low targets for diet of 0.31  $\mu\text{g/g dw}$  (EC0) and 1.0  $\mu\text{g/g dw}$  (EC05).

Once choices for modeling scenarios are made, the generalized equation for translation of a fish tissue Se concentration to water-column Se concentration (**Table 2 and Figure 7**) is

$$C_{\text{water}} = (C_{\text{fish}}) \div (\text{TTF}_{\text{fish}}) (\text{TTF}_{\text{invertebrate}}) K_d \quad (17)$$

where ( $K_d$ ) ( $C_{\text{water}}$ ) is substituted for  $C_{\text{particulate}}$  and the equation is solved for  $C_{\text{water}}$ . An analogous equation for translation of a bird egg Se concentration is

$$C_{\text{water}} = (C_{\text{bird egg}}) \div (\text{TTF}_{\text{bird}}) (\text{TTF}_{\text{invertebrate}}) K_d \quad (18)$$

Model scenarios and predicted allowable dissolved, suspended particulate material, and dietary Se concentrations for *C. amurensis*-based food webs are compiled in **Tables 17-18** and for aquatic insect-based food webs are compiled in **Table 19**. Food webs assume exposure of predators through a 100% clam diet or a 100% insect diet (see following section for mixed diet scenarios).  $K_d$ s are transect specific and TTFs are those listed above ( $\text{TTF}_{\text{clam}}$  for *C. amurensis* = 17.1;  $\text{TTF}_{\text{insect}}$  = 2.8;  $\text{TTF}_{\text{bird egg}}$  = 2.6;  $\text{TTF}_{\text{fish}}$  = 1.1).

Hydrologic conditions (residence time, water-year type, flow season, and NDOI, **Tables 17-19**) are listed because of their importance in determining processes that affect Se transformations between dissolved and suspended particulate material Se concentrations and the bioavailability of organic matter and Se to food webs (see additional discussion in *Choices, Limitations, and Reduction of Uncertainty* section). Modeling for a clam-based food web is limited to wet and above normal years because transects are not available for below normal, dry, or critically dry conditions. Landward modeling is

limited to above normal (January, 2003 and April, 2003) and below normal (October, 2003 and January, 2004) water years because of data availability. Modeling exposure for low flow seasons is emphasized here in illustrated scenarios. Low flow seasons (and especially low flow seasons during dry years) are considered critical times (i.e., *ecological bottlenecks*) that mainly will determine the ecological effects of Se on the estuary (Presser and Luoma, 2006). As discussed previously, **Figure 12** illustrates the importance of the low flow season in terms of cycles of prey Se contamination and habitat-use by species important to the Bay-Delta.

Modeling here predicts allowable Se concentrations that are linked to calculated  $K_{dS}$  across the estuary for individual transects (**Figures 23-25**). Thus, a Bay-Delta continuum approach can be used to generate a set of salinity-specific predictions. The theoretical constructs of predicted allowable dissolved Se concentrations illustrated in **Figures 23-25** are compared to observed dissolved Se concentrations in order to quantify the amount of reduction at a salinity-specific location, if needed, to meet assumed tissue guidelines for fish and birds. In a broader application, the approach generates means and ranges for dissolved and suspended particulate material Se concentrations across the estuary that can serve as an indicator to compare across time (**Tables 17-19; Figures 23-25**). As noted previously, use of a continuum mean may increase modeling uncertainty, but use of a continuum approach for modeling can give context for overall regulatory and management considerations by addressing salinity-specific locations.

Protection of fish for a seaward location is illustrated by specific exposure scenarios for an adult female white sturgeon (EC05 whole-body), a generic fish species (EC10 whole-body), and a juvenile white sturgeon (EC05 diet) under above normal water year and low flow season conditions (**Table 17; Figure 23**). Shown are: guidelines for whole-body fish; observed  $K_{dS}$  for November, 1999; and modeled dissolved, diet, and suspended particulate material Se concentrations (**Table 17**). Predicted allowed dissolved Se concentrations are shown across the salinity gradient and observed dissolved Se concentrations from the November 4-5, 1999 transect are given for comparison. All observed dissolved Se concentrations in November, 1999 exceed predicted allowable dissolved Se concentrations across the salinity gradient (**Table 17; Figure 23**).

Protection of aquatic birds at a seaward location is illustrated by specific exposure scenarios for a clam-eating bird species (EC05 diet and EC05 egg) and a generic bird species (EC10 egg) under above normal water year and low flow season conditions (**Table 18; Figure 24**). Both sets of scenarios are referenced to guidelines based on effects to mallards. As above, shown are: guidelines for bird eggs; observed  $K_{dS}$  for November, 1999; and modeled dissolved, diet, and suspended particulate material Se concentrations (**Table 18**). Predicted allowed dissolved Se concentrations are shown across the salinity gradient and observed dissolved Se concentrations from the November 4-5, 1999 transect are given for comparison. All observed dissolved Se concentrations in November, 1999 exceed predicted allowable dissolved Se concentrations (**Table 18; Figure 24**).

Protection of fish for a landward location is illustrated by specific exposure scenarios for a juvenile Chinook salmon (EC05 diet and EC05 whole-body) under two different transect conditions (below normal, low flow season; above normal, high flow season) (**Table 19; Figure 25**). As above, shown are: guidelines for whole-body fish; observed  $K_{dS}$  for October 10, 2003 and April 22-23, 2003; and modeled dissolved, diet, and suspended particulate material Se concentrations (**Table 19**). Predicted allowed dissolved Se concentrations are shown across the salinity gradient from Rio Vista and Stockton to Benicia and observed dissolved Se concentrations are given for comparison. Interpretation across these transects is complex given the interface with freshwater and the variation in  $K_d$ . For landward sites (categorized as Delta, **Figure 25**; see discussion below) during conditions in the low flow season of October, 2003, observed dissolved Se concentrations exceed predicted allowable dissolved Se

concentrations for fish whole-body targets of 1.5 and 2.4  $\mu\text{g/g dw}$  (**Figure 25**). For the furthestest landward sites during conditions in the high flow season of April, 2003, observed dissolved Se concentrations are less than predicted allowable dissolved Se concentrations for these targets (**Figure 25**).

Noted on **Figure 25** is a nominal division of Delta and Bay at Antioch, which is above Chipps Island. Data analysis and modeling for these transects assumes that an aquatic insect diet is consumed by fish even in habitats of higher salinity, a scenario that is unlikely. Additional data are needed to resolve food web questions such as this, along with monitoring at freshwater interfaces to better quantify and interpret the variation in location-specific  $K_{ds}$ . However, a broader point is proven by the results given in **Figure 25**: if the Bay supported an aquatic insect-based food web rather than a clam-based food web, then observed dissolved Se concentrations in the Bay would not be above predicted allowable dissolved Se concentrations during times and locations modeled here for the Bay.

Because of the importance of particulate material in determining food-web bioaccumulation, **Figure 26** shows observed and predicted suspended particulate material Se concentrations for the previously modeled exposure scenarios and set of guidelines (**Figures 23-25**). In addition, an exposure scenario for the estuary during June, 1998 (wet year, high flow season) is modeled (**Tables 17 and 18**). Patterns and ranges of particulate enrichment during a low flow season and high flow season are distinctly different and underlie the outcomes of overall exposure in modeling (also see *Choices, Limitations, and Reduction of Uncertainty* section). For seaward clam-based food webs during the low flow season in November, 1999, observed suspended particulate material Se concentrations exceed predicted allowable suspended particulate material Se concentrations (**Figure 26A**). For a seaward clam-based food webs during the high flow season in June, 1998 (an El Niño event), outcomes are varied for low salinity sites (**Figure 26B**). However, observed suspended particulate material Se concentrations exceed predicted allowable suspended particulate material Se concentrations at higher salinities (**Figure 26B**). For landward aquatic insect-based food webs (Delta) during October, 2003 (low flow season) and April, 2003 (high flow season), observed mean suspended particulate material Se concentrations exceed predicted allowable suspended particulate material Se concentrations for juvenile salmon, except at two low salinity locations (**Figure 26C**).

### Suisun Bay-Carquinez Strait

As previously described, a focused approach for Suisun Bay-Carquinez Strait uses compartmentalized data to narrow modeling to a specific location (**Figure 14**). Additionally, this site is especially impacted by oil refinery effluents. This narrowing of modeling eliminates some of the uncertainties associated with end-member processes (i.e., the variability at ocean-influenced and freshwater-influenced sites) that are part of the spectrum of the Bay-Delta. Landward sites can show the influence of elevated Se in allochthonous suspended particulate material and seaward sites can show the influence of amplified Se processing, a pattern seen in other estuaries (LeBlanc and Schroeder, 2008; Presser and Luoma, 2009) (**Figures 16, 17, 20**).

For modeling, a focused approach for Suisun Bay-Carquinez Strait lends itself mathematically to representation by a bounded range of parameter choices for regulatory consideration. Hence, modeling scenarios and predictions for *C. amurensis*-based food webs generated here illustrate the effect of a limited set of choices for Se effect guidelines,  $K_{ds}$ , and TTFs (**Tables 20 and 21**). As discussed previously, model choices can be altered to illustrate sensitivity to model parameters and uncertainties in model predictions under a range of regulatory or management actions. Comparative scenarios thus develop a range of predictions and identify data gaps and monitoring needs.

**Tables 20 and 21** show comparative prediction scenarios using a general set of Se effect guidelines for whole-body fish (8, 5, and 1.5 ppm dw) and for bird eggs (12, 7.7, 5.9 ppm dw) suggested through discussion with USEPA and USFWS. For Suisun Bay-Carquinez Strait, four choices for  $K_d$  are illustrated (mean  $K_d$ s of 1,180; 2,666; 3,435; and 5,986 during increasing residence times in low and high flow transects in 1998 and 1999) (**Tables 20 and 21**). Choices for  $TTF_{fish}$  are 0.8 and 1.1 and the choice for  $TTF_{bird\ egg}$  is 2.6. Choices for  $TTF_{prey}$  are:

- *C. amurensis*,  $TTF = 17$ ;
- mixed diet composite,  $TTF = 8.8$  (50% *C. amurensis*,  $TTF = 17$ ; 50% amphipod,  $TTF = 0.6$ );
- aquatic insect ( $TTF = 2.8$ ).

If a mixed diet composite  $TTF$  is used in modeling, then predicted prey Se concentrations also are composites that would need to be separated into individual components to assess allowable *C. amurensis* and amphipod Se concentrations. For example, if the predicted particulate Se concentration of  $0.826\ \mu\text{g/g}$  is derived using a  $TTF_{C. amurensis + amphipod}$  of 8.8, then allowable individual prey Se concentrations are

$$(0.826\ \mu\text{g/g}) (17) (0.5) = 7.02\ \mu\text{g/g}\ \text{for}\ C.\ amurensis,\ \text{and}$$

$$(0.826\ \mu\text{g/g}) (0.6) (0.5) = 0.25\ \mu\text{g/g}\ \text{for}\ \text{a}\ \text{generic}\ \text{amphipod}$$

for a sum of  $7.27\ \mu\text{g/g}$  as a composite prey Se concentration. Therefore, *C. amurensis* could not exceed  $7.02\ \mu\text{g/g}$  in this mixed diet composite scenario ( $TTF_{C. amurensis + amphipod}$ ) as compared to  $7.72\ \mu\text{g/g}$  in a scenario using a 100% clam diet ( $TTF = 17$ ). However, the predicted allowed particulate Se concentrations would be affected more significantly, with  $0.428\ \mu\text{g/g}$  allowed in the single species scenario and  $0.826\ \mu\text{g/g}$  in the mixed diet scenario. Overall though, the effect of this theoretical construct is to reduce the bioaccumulative potential of the modeled invertebrate species.

Modeling for the area of Suisun Bay-Carquinez Strait within the specified set of parameters listed above, gives ranges of predicted dissolved, suspended particulate material, and prey Se concentrations that can serve as the basis for regulatory consideration (**Tables 20 and 21**). Choices by regulatory agencies of necessary and sufficient combinations of model parameters will set the outcomes for criteria development and regulatory action in the future.

## Landward Sites

Comparative prediction scenarios also are generated from transects that focus on landward sites (Lucas and Stewart, 2007). Comparative outcomes from scenarios for aquatic insect-based food webs are illustrated in **Tables 22 and 23**. For a landward aquatic insect-based food web four choices for  $K_d$  are illustrated (means  $K_d$ s of 2,268, 2,981, 2,684, and 5,855 during low and high flow transects in 2003 and 2004) (**Tables 22 and 23**). Choices for predator  $TTF$ s are  $TTF_{fish} = 1.1$  and  $TTF_{bird\ eggs} = 2.6$ . As above, ranges of predicted dissolved, suspended particulate material, and prey Se concentrations can serve as the basis for regulatory consideration.

## Choices, Limitations, and Reduction of Uncertainty

Several figures throughout the report illustrate processes and outcomes important to the site-specific modeling approach used here for the Bay-Delta. These figures represent the fine-scale information that defines and quantifies the ecological, hydrodynamic, and biodynamic processes of the estuary that underlie and enable modeling. These figures include details of: sources and food webs (**Figure 2**); site-specific modeling approach (**Figure 9**); transformation and partitioning reactions ( $K_d$ ) (**Figure 13**); species and effects (**Figures 8, 10, 11, and 12**); and hydrodynamics during sampling of the estuary (e.g., **Figure 14**).

Presser and Luoma (2010) discuss the limitations of an ecosystem-scale modeling approach in general, but also note how models provide insights that advance understanding of value both to science and management. For the Bay-Delta, combining modeling with knowledge of fine structure estuary processes is important for reducing uncertainty and fortifying a mechanistic basis for modeling applications and predictions in the future. For example, **Figure 17** shows the effect of estuary processes on suspended particulate material Se concentrations during a low and a high flow season (April, 1999; November, 1999) across the Bay-Delta continuum. In further analysis of data for Suisun Bay-Carquinez Strait, **Figure 27** shows mean observed dissolved and suspended particulate material Se concentrations and  $K_d$ s as a function of residence time. Dissolved Se concentration decreases as residence time increases, but suspended particulate material Se concentrations increase sharply with increasing residence time. Including suspended particulate material Se concentrations and residence time as variables in **Figure 27** illustrates that transformation of dissolved Se to particulate Se (i.e., dissolved Se decreases as suspended particulate Se concentrations increase) occurs in the estuary as flow slows down (i.e., during increased residence time) as expected from theoretical considerations of Se phase dynamics (see previous discussion and Presser and Luoma, 2010). Given the steepness of the curve, regulation of suspended particulate material Se concentration may be a more sensitive parameter on which to assess change and choice. Defining or conceptualizing a baseline dissolved Se concentration or condition for the estuary is less certain because of the small dynamic range of dissolved Se concentrations.

If mean observed *C. amurensis* Se concentrations measured in samples from Suisun Bay-Carquinez Strait during the months surrounding the transect sampling are added to **Figure 27** to complete linkages of dissolved, particulate, and prey phases, then it is seen that *C. amurensis* Se concentrations also increase with increasing residence time (**Figure 27**). To further elucidate the efficiency of Se assimilation in this food web, **Figure 28** shows that the percentage of suspended particulate material organo-Se reaches 50% in both plots at a residence time of 22 days. Hence, the presence of a majority of organo-Se leads to efficient uptake into *C. amurensis* at increased residence times.

Thus, **Figures 27 and 28** inform the model as to 1) the fundamental underlying mechanistic linkage between hydrodynamics and Se dynamics in the estuary and 2) why scenarios should be tied to specific transformation and flow conditions (see also **Figure 9** for linked mechanistic components of model approach). Further, **Figure 27** helps establish the benefits of a  $K_d$ -approach in reducing uncertainties otherwise associated with modeling the complex processes of transformation and speciation, and of a biodynamic approach that incorporates the assimilation efficiency of particulate material.

## Data Collection, Model Updates, and Refinements

Current Data and Additional Modeling: Current data for dissolved, suspended particulate material, invertebrate, and predator Se concentrations (i.e., spatially and temporally matched datasets) are needed to update model predictions. Sampling and analysis would include Se concentrations for the dissolved phase; suspended particulate material; seaward bivalves and amphipods (or other seaward invertebrate species); aquatic insects (or other landward invertebrate species); sturgeon, salmon, steelhead (or other fish species); and eggs and tissue from avian species (see complete list in **Figure 11**). A designated set of methods for collection and analysis of samples used in modeling of the Bay-Delta are needed to add consistency to model inputs. Further documentation of a predator's dietary preference also would be desirable because food webs may change as criteria development goes forward. Follow-

up modeling can be done in response to collection of additional monitoring data and consideration of the pending USEPA national fish tissue guidance.

Representation of Hydrologic Conditions: Analysis of flow conditions to give context to the environmental partitioning and foodweb biodynamic processes described here is fundamental to modeling for the Bay-Delta. For example, transect data for wet and above normal water years illustrate how Se concentration, Se speciation, and  $K_d$  profiles vary during conditions in April, 1999 (a high flow season) as compared to November, 1999 (a low flow season) (**Figures 17 and 20**).

Below Normal, Dry, and Critically Dry-Year Low-Flow Conditions: Available seaward datasets do not include data from a below normal, dry, or critically dry year to model a clam-based food web. Hence, modeling here could not assess effects in the North Bay during times of low flow in a dry year (i.e., the *ecological bottleneck*) and locations where oil refinery Se effluents may exert their maximum effect. Available landward datasets do not include data from a dry year to model an insect-based food web. Comparing model predictions for scenarios based on a range of hydrologic conditions will help develop a more complete basis for regulatory guidance. The estuarine system is highly variable in terms of flow (**Figure 15**) because of management demands and the natural variability induced by climate.

Hydrodynamic Tracking of Se: A Se budget through the estuary is needed to differentiate sources and develop relationships to internal refinery sources and upstream river sources. For example, quantifying end-member Se concentrations for the Sacramento River and San Joaquin River would define the influence of riverine sources on Se concentrations in the estuary. Spatial and temporal definition in such a study should be such to resolve questions as future management strategies are implemented (**Figure 2**).

Chronic Effects in Birds: Modeling of clam-eating migratory bird species, such as scoter and scaup, in reference to potential chronic Se effects that may impact staging of diving ducks overwintering in the estuary (**Figures 8, 10 and 12**) would assess these species in scenarios relevant to the estuary use by these bird species.

Changes in Population Dynamics and Species Diversity: Monitoring and comprehensive compilation of data for community change, introduction of species, loss of species, and loss of individuals that are threatened or endangered would document changes to ecological pathways important to the sustainability and restoration of the estuary.

Site-Specific TTFs: Updated Se TTFs for *C. amurensis* could be calculated from modern matched datasets for suspended particulate material and bivalve Se concentrations. Biodynamic parameters could be investigated to further define bivalve kinetics. Modeling for *C. amurensis* also could be location-specific to add more specificity to modeling. Modeling could utilize  $TTF_{fish}$  of up to 1.9. Important site-specific Se TTFs to be updated include those for aquatic insects and other invertebrates that serve as food for landward food chains. Matched datasets for suspended particulate material and invertebrate Se concentrations would be needed.

Field-derived TTFs for bird species: Field-derived TTFs for bird species (and other predators) would encompass habitat use and other factors that influence exposure.

Particulate Material Se Concentrations: In modeling, derivation of a particulate Se concentration can be very site-specific as defined by the monitoring data available for modeling. This type of refinement to model parameters is discussed in Presser and Luoma (2010). For example, a concentration of Se in food can be calculated that takes into account site-specific bioavailability of particulate material to invertebrates. The generalized equation is

$$C_{particulate} = (AE) (C_{particulate\ a}) (\text{sediment fraction}) + (AE) (C_{particulate\ b}) (\text{detritus fraction}) + (AE) (C_{particulate\ c}) (\text{algae fraction}) \quad (19)$$



In terms of suspended particulate material as used for Bay-Delta modeling, a composite assimilation efficiency can be derived (see equation 15) to adequately represent food for clams.

**Mixed Diet:** Rather than assuming a 100% clam-diet for predators, allowable dissolved Se concentrations could be calculated using the equation for a mixed invertebrate diet

$$C_{\text{water}} = (C_{\text{fish}}) \div (\text{TTF}_{\text{fish}}) (K_d) [(\text{TTF}_{\text{invertebrate a}}) (\text{prey fraction})] + [(\text{TTF}_{\text{invertebrate b}}) (\text{prey fraction})] + [(\text{TTF}_{\text{invertebrate c}}) (\text{prey fraction})] \quad (20)$$

The percentage of clam in the diet of species at risk (**Figure 11**) could be used specifically. A choice as to the percentages of other types of invertebrates in the diet of each predator and a  $\text{TTF}_{\text{invertebrate}}$  would need to be developed or assumed from literature sources for each additional invertebrate modeled.

**Longer Food Webs:** For fish-eating birds or the bald eagle food webs, model scenarios could incorporate sequential bioaccumulation in longer food webs

$$C_{\text{water}} = (C_{\text{fish}}) \div (\text{TTF}_{\text{fish}}) K_d (\text{TTF}_{\text{invertebrate}}) (\text{TTF}_{\text{forage fish}}) \quad (21)$$

$$C_{\text{water}} = (C_{\text{fish}}) \div (\text{TTF}_{\text{fish}}) K_d (\text{TTF}_{\text{TL2 invertebrate}}) (\text{TTF}_{\text{TL3 invertebrate}}) (\text{TTF}_{\text{TL3 fish}}) \quad (22)$$

For example, modeling a Dungeness crab food web would constitute an additional bioaccumulative step when juveniles are consumed by large predator fish or adults are consumed by mammals (**Figure 11**).

**Specificity for Low-Salinity Locations:** As noted previously, low-salinity locations were not sampled on a consistent basis for the Bay-Delta during the analysis periods reported on here.

Designation of specific sampling locations would greatly improve predictions for landward sites. Data analysis that compares dissolved and suspended particulate material Se concentrations and calculated  $K_d$ s at specific locations across time also would be helpful to regulatory guidance. Datasets specific to Se concentrations in landward food webs (e.g., invertebrates and salmonids) need to be collected because the current record is inadequate.

**Reference Dose Methodology Comparison:** Ecosystem-scale modeling here is applicable to using a dietary Se concentration as a regulatory guideline. The USFWS provided, in some cases, both tissue and diet Se concentrations as effects levels. An alternative approach would be to calculate a dietary Se concentration or dose for aquatic wildlife based on a protective reference dose and specific body weights of predators (USFWS, 2003; Presser and Luoma, 2010). Validation would be important; uncertainties in the relationship of body weight and ingestion rate, for example, would need to be considered. Results of this analysis could be compared to those outcomes of modeling scenarios shown here to add weight to the conclusions drawn for the protection of predators in the Bay-Delta estuary. Steps like this in the methodology could also serve to harmonize regulation, a goal long sought in obtaining consensus and understanding (Reiley et al., 2003).

**Data Analysis:** Ecosystem-scale modeling is more than mathematical correlations. Its success, in part, depends on formalization and conceptualization of existing data for food web ecology, system hydrology, and the biogeochemistry of partitioning. Thus, ultimately a comprehensive Bay-Delta model (i.e., addressing interconnection of estuarine processes, habitats, species, and stressors) as originally conceived by CALFED, would help with details of species, habitat use, competing contaminants, and estuary hydrodynamics.

## Conclusions

Analysis from the biodynamically-based methodology for ecosystem-scale modeling as presented in Presser and Luoma (2010) showed, in general, that:

- a crucial factor ultimately defining Se toxicity is the link between dissolved and particulate phases at the base of the food web (i.e.,  $K_d$ );
- collection of particulate material phases and analysis of their Se concentrations are key to representing the dynamics of the system;

- bioaccumulation in invertebrates is a major source of variability in Se exposure of predators within an ecosystem, although that variability can be explained by invertebrate physiology (i.e.,  $TTF_{\text{invertebrate}}$ );
- $TTF_{\text{fish}}$  is relatively constant over the range of species considered here; and
- Se concentrations are at least conserved and usually magnified at every step in a food web.

In addition, an ecosystem-scale approach: 1) clearly documents pathways that connect dissolved Se to bioaccumulated Se in species of concern; 2) provides a record of supporting data on which to base decisions; 3) uses site-specific ecology, biogeochemistry, and hydrology; 4) includes choices explicitly throughout the decision-making process; 5) addresses uncertainties by showing outcomes of different choices in modeling scenarios; and 6) validates outcomes through comparison to field data.

A site-specific methodology for development of Se criteria for the Bay-Delta includes the following steps:

- identification of predators at risk and their critical life stages;
- development of conceptual food-web models for predators at risk that include dietary preferences (i.e., percentages of species of invertebrate consumed);
- development of seasonal-cycle and habitat-use diagrams for prey and predators at risk;
- derivation of tissue guidelines for species at risk specific to exposure route, effect endpoint, and magnitude of effect (EC0, EC05, and EC10);
- analysis of spatially and temporally matched datasets for dissolved and suspended particulate material Se concentrations across the salinity gradient;
- derivation of salinity-specific or location-specific  $K_d$ s;
- derivation of site-specific  $TTF_{C. \text{ amurensis}}$ ;
- selection or development of  $TTF_{\text{fish}}$ ,  $TTF_{\text{bird}}$ , and TTFs for other invertebrates;
- validation of modeling through comparison of predictions to observed Se concentrations;
- development of exposure scenarios specific to location and season or residence time; and
- prediction of allowable dissolved, suspended particulate material, and prey Se concentrations.

Consideration of compliance with allowed Se concentrations across media (i.e., water, particulate, prey and predator) harmonizes regulation and is a measure of ecological consistency and relevance of the links among exposure, transfer, and effects.

Modeling here for a seaward *C. amurensis*-based food web is referenced to data from transects from November, 1997 to November, 1999. Modeling for a landward aquatic insect-based food web is referenced to data from transects from January, 2003 to January, 2004 from Rio Vista and Stockton to Benicia. USFWS effect guidelines and associated levels of protection are used in modeling to predict toxicity under different regulatory proposals. Validation of the model shows the model is able to generate 1999-2000 seaward conditions for Se concentrations in a *C. amurensis* to white sturgeon food web and 2003 landward conditions for Se concentrations in an aquatic insect to largemouth bass food web.

Site-specific analysis and modeling show that:

- estuarine approaches that focus on seaward, landward, and Suisun Bay-Carquinez Strait locations can illustrate influences of site, time, and flow-specific partitioning conditions;
- choices of geographic constraints, species, diet, and estuary conditions all are influential in risk management for Se;
- the field-derived  $TTF_{C. \text{ amurensis}}$  that is derived here is the first instance of a field-derived TTF for a marine bivalve species; the value is appreciably higher than laboratory-derived values;
- modeling of species at risk takes into account both inherent sensitivity and potential exposure;

- a *C. amurensis*-based food web in the estuary is highly vulnerable to Se inputs because of high potential exposure;
- regulation of suspended particulate material Se concentration may be a more sensitive parameter on which to assess change and choice because of the small dynamic range of dissolved Se concentrations in the estuary; and
- critical ecological times are functionally connected to the underlying dynamics and processes of low flow periods in Suisun Bay-Carquinez Strait thus allowing modeling and prediction as changes occur in management and regulations.

The approach could be refined by:

- collecting modern matched datasets for water, suspended particulate material, invertebrates, fish, and birds as illustrated in **Figure 11**;
- determining contributions of specific sources;
- quantifying end-member Se concentrations and their hydrodynamic connection to estuary Se concentration;
- further limiting geographic (e.g., Suisun Bay) and temporal constraints (dry year, low flow season);
- analyzing processes at interfaces of freshwater/bay/ocean;
- addressing biodynamics of Se and chronic toxicity in avian species; and
- further linking ecosystem-scale modeling to fine structure estuary processes.

Analysis of Se concentration and speciation for characterized particulate phases are practical measures of the complex water/sediment/particulate *milieu* that forms the base of the food web and is consumed as food by invertebrates. Future monitoring to increase the suspended particulate material database under a suite of flow conditions would enhance our understanding of estuarine transformation. Monitoring invertebrate Se concentrations in food webs also is a practical, informative step in monitoring because the first and second most variable aspect of Se dynamics (i.e.,  $K_d$  and  $TTF_{\text{invertebrate}}$ ) are integrated into invertebrate bioaccumulation.

Expressly for modeling of avian species, uncertainties exist around biodynamic modeling parameters ( $TTF_{\text{bird egg}}$ ); movement and migration; and links of bioaccumulation, exposure, and toxicity under site-specific conditions. Additionally, modeling of overwintering clam-eating migratory bird species, such as scoter and scaup, based on potential chronic Se effects that may impact staging bird would assess these species in scenarios relevant to their use of the estuary. Chronic toxicity effects include:

- compromised body condition (low body mass);
- oxidative stress (increased susceptibility to disease as immune system is suppressed);
- decreased winter survival;
- decreased reproductive fitness (decreased breeding propensity, reduced recruitment) and;
- behavioral impairment (missed breeding window, delayed timing of departure).

Predictions from a reference dose methodology for birds also would strengthen outcomes for protection of avian species.

In sum, the amount of available data for the Bay-Delta may be limited, especially under below normal, dry, and critically dry year conditions, but given the specificity of Se processes and food web species that is documented and modeled here, enough is known about the biotransfer of Se and the interconnectedness of habitats and species to set a range of limits and establish an understanding of the relevant conditions, biological responses, and ecological risks critical to management of the Bay-Delta. Site-specific modeling here bounds predictions within spatial and temporal components and quantifies key characteristics of the system that can influence exposure and uptake of Se by fish and birds. The

uncertainty that stems from the variability in these processes reflects the complexity of the estuary. Nevertheless, the methodology used here is able to document fine-structure processes in different habitats and provide context for future scenario development. The greatest strength of the analytical and modeling processes is that it is an orderly, harmonized derivation approach across media for assessing different choices of Se criteria for protection of fish and birds.

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