

**NORTH SAN FRANCISCO BAY
SELENIUM CHARACTERIZATION
STUDY PLAN
(2010–2012)**

**WESTERN STATES PETROLEUM
ASSOCIATION**

OCTOBER 28, 2010



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Senior Coordinator, Bay Area and State Water Issues

VIA ELECTRONIC MAIL

April 25, 2011

Erin Foresman
US Environmental Protection Agency
75 Hawthorne Street
San Francisco, CA 94105

Subject: Water Quality Challenges in the San Francisco Bay/Sacramento-San Joaquin
Delta Estuary (Document ID EPA-R09-OW-2010-0976-0001)

Dear Ms. Foresman,

The Western States Petroleum Association (WSPA) is a non-profit trade association representing twenty-six companies that explore for, produce, refine, transport and market petroleum, petroleum products, natural gas and other energy supplies in California, Arizona, Nevada, Oregon, Washington and Hawaii.

In response to the Advanced Notice of Proposed Rulemaking (ANPR) for Water Quality Challenges in the San Francisco Bay/Delta Estuary (Bay Delta Estuary), we are providing the attached comments.

The focus of our comments pertains to selenium in the Bay Delta Estuary. The San Francisco Bay Regional Water Quality Control Board has completed preliminary efforts on their development of the North San Francisco Bay Selenium Total Maximum Daily Load (TMDL). The TMDL incorporates several documents that are included as supporting documents to our comments: Technical Memorandum 2 (TM-2) Selenium Data Summary and Source Analysis; Technical Memorandum 3 (TM-3) Toxicological Assessment; and, Technical Memorandum 6 (TM-6) Simulation of Selenium Fate and Transport.

In addition, the North San Francisco Bay Selenium Characterization Study (Study) is currently underway, and the work plan is included as a supporting document. This Study in conjunction

with the results presented in TM-6 provides the basis for a reevaluation of selenium speciation in the Bay after a data collection gap of nearly 10 years.

The information from the TMDL and Study indicates that the ratio of particulate to dissolved selenium concentrations (K_d) cannot be assumed to remain fixed over changing conditions, which may include, among other things, changing sources, phytoplankton abundance and species, selenium speciation, and also seasonal and long term hydrological changes. The transformations and uptake of various selenium species in the Bay Delta Estuary have been shown to be dynamically complex, and thus the use of a simple predictive tool to assess uptake would not be appropriate.

The model developed in the TMDL has demonstrated the ability to predict selenium concentrations in the water column and associated bioaccumulation in water body biota. The model was verified using clam data collected from 1995 – 2010 and was shown to accurately simulate the long-term record of selenium in the clam *Corbula amurensis*; this clam is described in the ANPR as a selenium-sensitive species. The ability to explain these clam data is a key advantage of the use of a more process oriented model that can be applied in settings where there are many changing factors, and where the assumption of a constant K_d ratio is not valid.

The attachments to our cover letter provide greater detail on these and other key issues we believe are vital to establishing a more accurate understanding for any proposed regulatory development pertaining to selenium in the Bay Delta Estuary that EPA may consider. Our comment package incorporates a Summary of Responses (Summary) to the three questions posed in the ANPR, detailed comments that provide expanded content to the Summary, and supporting documents from the Selenium Characterization Study and the TMDL.

We look forward to EPA's review of our comments, completing its evaluation, and providing the results of its review to the public. Thank you for this opportunity to provide input on this important matter.

Sincerely,



Attachments:

Supporting Information in Response to Water Quality Challenges in the San Francisco Bay/Sacramento-San Joaquin Delta Estuary, Unabridged Advanced Notice of Proposed Rulemaking

North San Francisco Bay Selenium Characterization Study Plan (2010 – 2012)

Technical Memorandum 2. North San Francisco Bay Selenium Data Summary and Source Analysis

Technical Memorandum 3. North San Francisco Bay Selenium Toxicological Assessment

Technical Memorandum 6. Application of ECoS3 for Simulation of Selenium Fate and Transport in North San Francisco Bay

Supporting Information in Response to Water Quality Challenges in the San Francisco Bay/Sacramento-San Joaquin Delta Estuary, Unabridged Advanced Notice of Proposed Rulemaking

Prepared by Tetra Tech, Inc.

April 25, 2011

Summary of Responses

A review of the information summarized by the U.S. Environmental Protection Agency (EPA) within the Selenium Program Area of the *Unabridged Advanced Notice of Proposed Rulemaking* is presented in the attached technical document. Detailed responses are presented for three questions presented by EPA for public comment. New information, contributing to the understanding of the behavior of selenium in the Bay Delta Estuary, is presented from the ongoing North San Francisco Bay Selenium Characterization Study. This study will continue through 2012 and will provide vital new information on the sources of selenium and the seasonally-influenced physical and chemical factors that affect selenium behavior in the Bay Delta Ecosystem. As part of the supporting activities provided for the development of a selenium TMDL for North San Francisco Bay, a numerical model of selenium fate and transport has been developed. This model accounts for the complex behavior of dissolved and particulate selenium in the Bay Delta Estuary and accounts for the relative efficiency of food webs in concentrating selenium. Within the technical responses below, the results of new model simulations are presented that accurately simulate the long-term record of selenium in the clam *Corbula amurensis*, described in the ANPR as a selenium-sensitive species. The responses to the posed questions also include recommendations for data needed to track selenium impacts in the Bay Delta Ecosystem. These data needs include 1) Delta selenium concentrations, 2) *Corbula amurensis* selenium concentrations and abundance, 3) particulate selenium concentrations at the ocean boundary, 4) selenium concentrations in higher trophic levels, and 5) a sustained selenium modeling framework. Additionally, this response provides a review of existing toxicity data interpretations and presents information regarding selenium's protective effects related to methylmercury toxicity.

Summary of Question Responses

- 1.0 What, if any, additional information is available to better characterize selenium sources, loadings and impacts within the watershed of the Bay Delta Estuary?

New Selenium Source Characterization Data

The *North San Francisco Bay Selenium Characterization Study (2010–2012)* is underway with the second of four sampling events completed in March 2011. Three types of samples are collected and analyzed: (1) Transect samples collected along a salinity gradient in the estuary, including locations in the Sacramento and San Joaquin Rivers, (2) Refinery effluent receiving-water samples collected near the effluent outfall to characterize near-field selenium concentrations and speciation; and, (3) Refinery effluent samples collected at a fully treated effluent discharge location.

The new data collected in the Selenium Characterization Study provide the basis for a major reevaluation of selenium speciation in the bay after a gap of 10 years. The data obtained in this work can be compared directly with the prior sampling, and allow interpretation of changes over the preceding decade. The preliminary findings show that K_d values, representing the ratio

of particulate to dissolved concentrations, are lower in 2010 than in 1999 by a factor of 2 to 3 (Figure ES-1). This is a significant finding and demonstrates the complexity of selenium uptake by different living and non-living particulate phases. These calculations show:

- that any given snapshot of selenium distribution in different compartments should be treated with caution, and
- that the ratio of particulate to dissolved cannot be assumed to remain fixed over changing conditions, which may include, among other things, changing sources, phytoplankton abundance and species, selenium speciation, and also seasonal and long term hydrological changes.

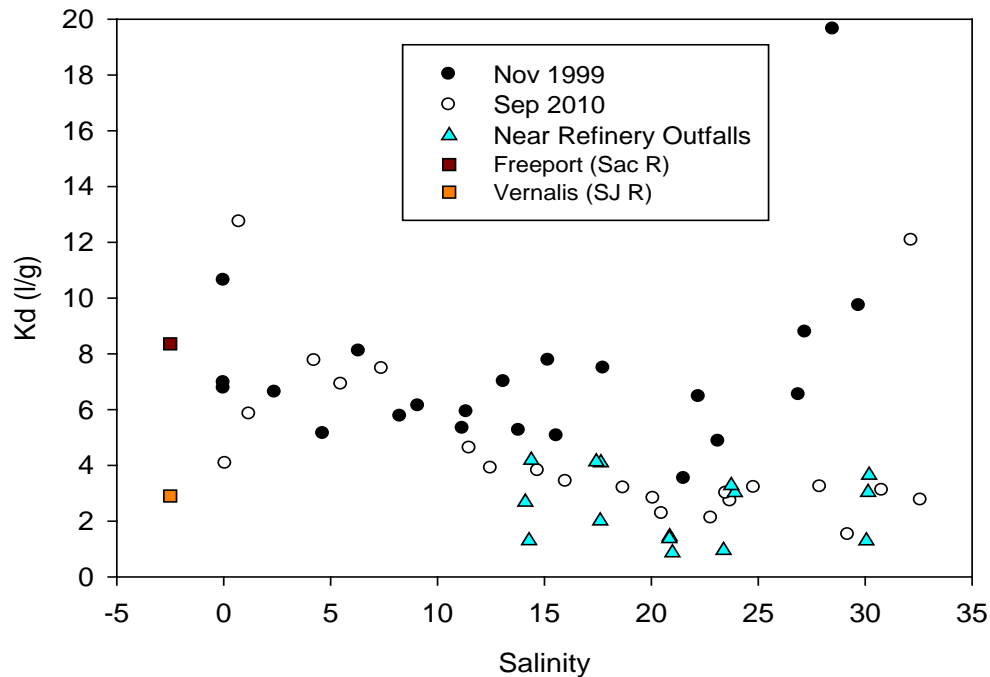


Figure ES-1. Ratio of particulate to dissolved selenium concentrations (expressed as Kd) across the estuary with data from November 1999 and September 2010.

Existing Toxicity Data and the Evaluation of Selenium Impacts

With the effort that is underway by EPA to develop a water quality criterion based on fish tissue concentration, it is important to take a critical look at the key studies that contribute to the selenium toxicity information in general and the information for species considered for evaluation of selenium exposure risk in the Bay Delta. Toxicity information for two species, white sturgeon (*Acipenser transmontanus*) and Chinook salmon (*Oncorhynchus tshawytscha*) is presented in the detailed response to questions. Additionally, new information is presented on the potential protective effects of selenium against methylmercury toxicity. The primary findings are:

- Unpublished laboratory studies using the white sturgeon have established a link between Se in parental fish tissue being transferred to eggs and larvae and resulting in substantial deformities at concentrations above about 25 ug/g. Based on these same

studies, some investigators have attempted to identify either effect levels or No Observable Effect Concentrations (NOECs) that inherently have high variability and are not defensible based on the data reported.

- The USFWS has concluded that a tissue concentration in the Chinook Salmon of 7.9 µg/g would result in 15% mortality within 10 days. There are several issues associated with this interpretation of previously published data identified in the full response to questions. Further, it is not defensible to base a criterion on a 15% effect because this is statistically and ecologically highly uncertain.
- Dietary selenium has been shown to provide protective effects against methylmercury toxicity. There is a high binding affinity between selenium and mercury, and the mercury-selenium complexes formed have low solubility. As a result, the mercury-selenium present in tissues of prey species may not be available for dietary absorption. This relationship between mercury and selenium should be investigated further in the characterization of selenium impacts in the Bay Delta.

2.0 What data, studies, and analytical techniques (for example, models) could be used to improve our understanding of the physical processes, including surface-groundwater interactions, controlling selenium mobilization and transport to and within the Bay Delta Estuary?

Selenium exists in multiple dissolved and particulate species, with transformations between them. In the Bay Delta Estuary, these transformations are overlaid on variable riverine and tidal influences. Of the different species, particulate selenium species are of most interest, due to its sequestration by clams, and further uptake by predator organisms. Selenium speciation and thus biological uptake varies on annual and seasonal time scales. Simple representations have been proposed for biological uptake, principally by assuming that particulate selenium is a ratio of the dissolved selenium (represented as a value of K_d , as noted in the answer to the previous question). However, this approach does not capture the changing selenium speciation in the Bay and does not explain the variations in clam concentrations that have been observed over the last 15 years. Given this limitation, the simple K_d -based approach may not be able to project future clam concentrations, especially when there are changes in the hydrologic drivers, such as modifications in the flows through the Delta, or changes in the mix of Sacramento and San Joaquin River inflows.

In support of the North San Francisco Bay (NSFB) Selenium TMDL, a more detailed evaluation of the selenium fate and transport processes was developed, including characterization of all known sources, and evaluation through a modeling framework that accounts for the various transformation and uptake processes. The goal of this effort was to develop a linkage between sources, water column concentrations, and biota concentrations that represents the best current understanding of underlying processes.

As a first step, loads were characterized from all known point and non-point sources, and from various existing data sources. Annual loadings from the Central Valley through the Delta are the largest source of selenium with high variability depending on total flow through the Delta. Loads

in high flow years are estimated to be more than ten times higher than in low flow years. The average Delta load is estimated to be 3,962 kg/yr. Local tributaries draining both urban and non-urban areas, although contributing lower flows than the Sacramento and San Joaquin Rivers, have high selenium concentrations, and are also a large source of selenium during the wet months (estimated average load of 354-834 kg/yr). Refineries are estimated to contribute ~550 kg/yr to NSFB.

To represent selenium processes, an estuary model was used to simulate the selenium concentrations in the water column and bioaccumulation of selenium in the NSFB (ECOS3 model, Harris and Gorley, 2003). The model built upon the previous work of Meseck and Cutter (2006) and was applied in one-dimensional form to simulate several constituents including salinity, total suspended material (TSM), phytoplankton, dissolved and particulate selenium, and selenium concentrations in bivalves and higher trophic organisms. Selenium species simulated by the model include selenite, selenate, and organic selenide. The particulate species simulated by the model include particulate organic selenium, particulate elemental selenium, and particulate adsorbed selenite and selenate.

The modeling shows that dissolved concentrations vary over a narrow range in both the dry and wet weather days, and are accompanied by significant changes in the particulate selenium speciation and K_d values in space and across seasons. This is explained as follows: In the dry season, the contribution of riverine particulate selenium is small relative to the in situ generation of phytoplankton. These conditions also result in higher particulate selenium concentrations (in $\mu\text{g/g}$). In the wet season, the contribution of riverine particulates is larger relative to in situ generation, and the overall particulate composition is more mineral and lower in selenium concentration. Furthermore, the mineral-rich particulates in greater abundance during the wet season are also assimilated less efficiently by clams. Riverine contributions of particulate selenium change from year to year, with resulting changes in concentrations of particulate selenium in the Bay, i.e., wet years have a greater riverine influence, and greater abundance of mineral-Se particulates.

The model above is especially important in explaining the clam data collected from 1995-2010, and which exhibit significant seasonal and inter-annual variability. The modeled concentrations of clams are shown along with the annual data in Figure ES-2. The model was applied using measured riverine inflows, as well as using the calibrated parameters for selenium transformation based on the 1999 speciation data, and uptake rates and assimilation efficiencies for different selenium species. A reduction in point source loads, through improved refinery wastewater treatment, is also included in the model inputs. Overall, the model is able to describe key features in the clam concentration behavior accurately. Changes from the dry season (high concentrations) to the wet season (low concentrations) in each annual cycle are explained by the riverine input of mineral-Se with lower concentrations and lower assimilation efficiency. Changes in clam selenium concentrations from one year to the next are influenced significantly by hydrology, with wet years (such as 2005 and 2006) resulting in lower clam concentrations. The ability to explain this temporal clam behavior also provides insight into future changes in the Bay, where flow modifications in the San Joaquin River or the Delta may result in riverine inputs that differ from historical, both in volume and in the amount of particulate selenium represented by the relative proportion of Sacramento and San Joaquin River flows.

The use of this model addresses the need identified in Question 2 to better explain selenium processes controlling selenium mobilization and transport to and within the Bay-Delta Estuary. Although more complex than a ratio-based approach, the added benefit of explaining mechanistically an important process of selenium uptake in the system, makes this an important tool in assessing future changes over the long term.

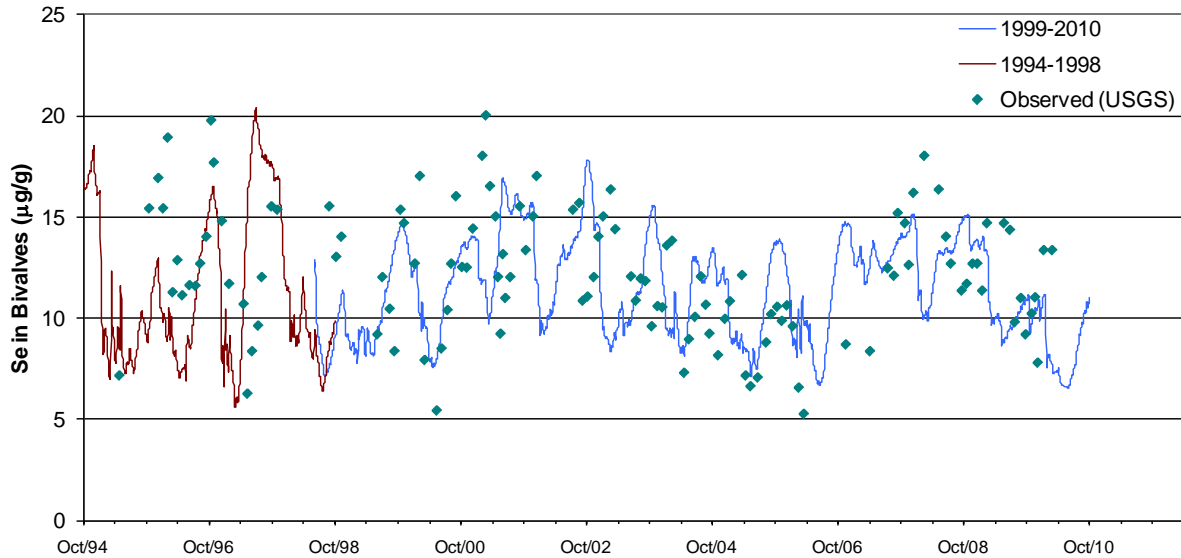


Figure ES-2 Simulated selenium concentrations in bivalve *Corbula amurensis* compared to long-term data from USGS at the Carquinez Strait for the period of 1994-2010 (Kleckner et al. 2010). Flow data used: DAYFLOW records; Refinery data used: daily data for 1999-2007, constant loads after 2007; San Joaquin River Selenium: observed data at Vernalis, multiplied by Delta removal constants.

3.0 What data are needed to track selenium impacts in the Bay Delta ecosystem as currently configured, and to evaluate potential impacts of selenium under changed flow and transport conditions into and within the Delta?

There is a critical need to develop a focused data collection effort to develop information: 1) to establish existing conditions in the Bay Delta with respect to the effects of selenium, 2) to serve as a basis for measuring change to the system, and 3) to gauge the effects of ecological forcing factors such as changes in food-web structure, flow conditions, and differences sources and forms of selenium to the system. Only recently with the implementation of the Selenium Characterization Study has there been a field sampling program devoted to supporting the development of selenium regulations. Without the collection of additional field and laboratory data, there is a risk of selecting model parameter values from sparse or incomplete data sets that support the existing concepts regarding both the relative importance of factors that affect the Bay Delta ecosystem and the existence of impairment.

The critical data needs are best classified into the following topics:

- **Delta selenium concentrations.** The Bay currently receives its largest selenium load from the Delta, which reflects the mixing of the Sacramento and San Joaquin Rivers, the export of a significant fraction of selenium through the aqueducts, and the transformation and uptake of selenium in the Delta. However, the behavior of selenium in the Delta has been inadequately monitored, and the process-level understanding is limited. A regular monitoring program that includes selenium speciation through a network of stations in the Delta is important to implement.
- ***Corbula amurensis* selenium concentrations and abundance.** The elevated risk of selenium to benthic feeding organisms is strongly tied to efficient uptake by the invasive clam, *Corbula amurensis*. Concentrations in this clam provide a useful indicator of selenium in bay particulates, and it is important that this monitoring be continued in the foreseeable future. At present, these data are not routinely released to the public, and the 1995-2010 were only recently released. Easier access to these data, perhaps on an annual basis would make these more useful to the Bay Delta scientific community and allow interpretation of the influences of selenium loads and hydrology on possible uptake.

There is also little publicly reported information on its abundance of *C. amurensis* over time. A monitoring program that reports on the abundance of these organisms in units of biomass per unit area, would provide valuable information on the potential contribution to the diet of benthic feeding species.

- **Ocean boundary conditions.** Besides the Delta, another important source of relevance to particulate selenium in the Bay is concentrations in the Pacific Ocean beyond the Golden Gate Bridge. Measurement of ocean particulate selenium values is part of the 2010-2012 sampling plan of the Selenium Characterization Study, but longer term monitoring of this boundary is also recommended.
- **Higher trophic level organism data.** One of the key indicators of impairment due to selenium in the Bay-Delta is the concentration of selenium in the muscle tissue and/or liver of the white sturgeon. However, there is insufficient data to evaluate either the existence of impairment or the evaluation of trends. Moreover, with the apparent enhanced selenium bioaccumulation ability of the clam *Corbula amurensis* it is necessary to quantify the importance of this species to the mixed diet of the white sturgeon.
- **Ongoing selenium modeling support.** Over time, selenium transport cycling in the bay is expected to change, driven by hydrologic variability, Delta modifications, land use changes in the watershed, changing algal species and abundance, and possible changes in the distribution of organisms in the bay. Sustained support of a modeling framework that ties together these elements and can be tested against the data should be an important component of the overall monitoring strategy for the Bay.

Supporting Information in Response to Water Quality Challenges in the San Francisco Bay/Sacramento-San Joaquin Delta Estuary, Unabridged Advanced Notice of Proposed Rulemaking

This document provides responses corresponding to questions identified in the Advanced Notice of Proposed Rulemaking (ANPR) related to selenium on page 29 (referring to the February 2011 unabridged version of the ANPR). The three questions that are supported with new information include the following:

1. What, if any, additional information is available to better characterize selenium sources, loadings and impacts within the watershed of the Bay Delta Estuary?
2. What data, studies, and analytical techniques (for example, models) could be used to improve our understanding of the physical processes, including surface-groundwater interactions, controlling selenium mobilization and transport to and within the Bay Delta Estuary?
3. What data are needed to track selenium impacts in the Bay Delta ecosystem as currently configured, and to evaluate potential impacts of selenium under changed flow and transport conditions into and within the Delta?

In the text below an overview is provided of key data that is relevant, including a review of previously published information related to water quality, biota concentrations, and toxicity, as well as key results of a numerical process model and an updated conceptual model of selenium uptake processes in the Bay Delta Estuary. Through this information an explanation is provided for the patterns of clam concentrations in the Bay that are referred to in the ANPR, but without an explanation of the underlying processes. A summary is also provided of new selenium data currently being collected in North San Francisco Bay (NSFB), constituting a major reevaluation of selenium speciation in bay after a gap of ten years. This additional body of information offers valuable insight into the behavior of selenium in the Bay, particularly the influence of long-term, regional-scale changes, such as relating to hydrologic patterns, changing Delta water exports in aqueducts, as well as modification of flows through the Delta to the Bay.

Responses below are grouped according to the questions in the ANPR. More detailed information is provided in a set of technical reports that were earlier prepared in support of the selenium TMDL in NSFB. Electronic versions of these reports are attached to this submission.

1.0 What, if any, additional information is available to better characterize selenium sources, loadings and impacts within the watershed of the Bay Delta Estuary?

Overview of Data Presented

A summary of an ongoing selenium water quality data collection effort in the Bay and Delta and an analysis of toxicity of selenium relevant to fish species found in San Francisco Bay is presented below. The water quality data in particular represent a major new effort at characterizing selenium distribution and speciation in North San Francisco Bay, as well as major external influences, such as the inflows from Sacramento and San Joaquin Rivers, and the oceanic influence beyond the Golden Gate Bridge.

New Selenium Source Characterization Data

The Regional Water Board's 2010 Amendment of Waste Discharge Requirements for San Francisco Bay Region Refineries, Order R2-2010-0057, was adopted in March 2010. It directed the refineries to implement effluent and receiving water selenium characterization studies as set forth in Table 4 of the Order.

The *North San Francisco Bay Selenium Characterization Study Plan (2010–2012)* prepared by the Western States Petroleum Association (WSPA, 2010) provided a detailed description of the number and location of samples, the laboratory analytical methods, and the reporting requirements associated with the characterization study. The Study Plan describes two wet weather and two dry weather sampling events over the two-year (2010-2012) sampling program. The first dry weather and wet weather sampling events were successfully conducted in September 2010 and March 2011, respectively.

The purpose of this report is to summarize the 2010 dry weather findings and compare them to data generated in the 1999 North San Francisco Bay using the same methods. The wet weather samples are currently being analyzed by Dr. Greg Cutter (Old Dominion University).

Study Plan Description

The Study Plan (WSPA, 2010) describes the three types of samples that are required to be collected and analyzed: (1) Transect samples collected along a salinity gradient in the estuary, including locations in the Sacramento and San Joaquin Rivers, (2) Refinery effluent receiving-water samples collected near the effluent outfall to characterize near-field selenium concentrations and speciation; and, (3) Effluent samples collected at a location equivalent to the existing effluent compliance point.

First Year of Water Quality Sampling

The dry weather field sampling of transect and receiving water stations occurred on September 8–13, 2010. Refinery effluent monitoring has taken place on a monthly basis, beginning in September, 2010. Each of these sampling activities is described below.

Transect – Transect samples were collected from 22 sites between a site near the Golden Gate Bridge and the Sacramento River at Rio Vista, CA and the San Joaquin River at USGS gage 757 along salinity increments of approximately 1.5-2 parts-per-thousand (g/l); providing a range of salinities from marine (33 g/l) to fresh (<1 g/l).

Samples were also collected on the Sacramento River at Freeport and on the San Joaquin River at Vernalis. The objective of these samples was to establish new endpoint locations that will be used to establish the boundary conditions for the modeling and analysis efforts.

Refinery Effluent Receiving Water – The objective of the receiving-water sampling is to characterize the mixing characteristics of the discharge and the speciation of the selenium upon initial dilution in the receiving water. Samples were collected from the outfall of each refinery’s diffuser. The diffusers are located approximately perpendicular to the flow direction, which changes over time as currents reverse over tidal cycles. Receiving water samples were collected from the zone of initial dilution (ZID) for each discharge, with one being approximately 10m up current and another being approximately 10m down current of each refinery’s discharge for a total of three sample locations per diffuser.

The locations of the dry weather sampling stations are presented in Figure 1.

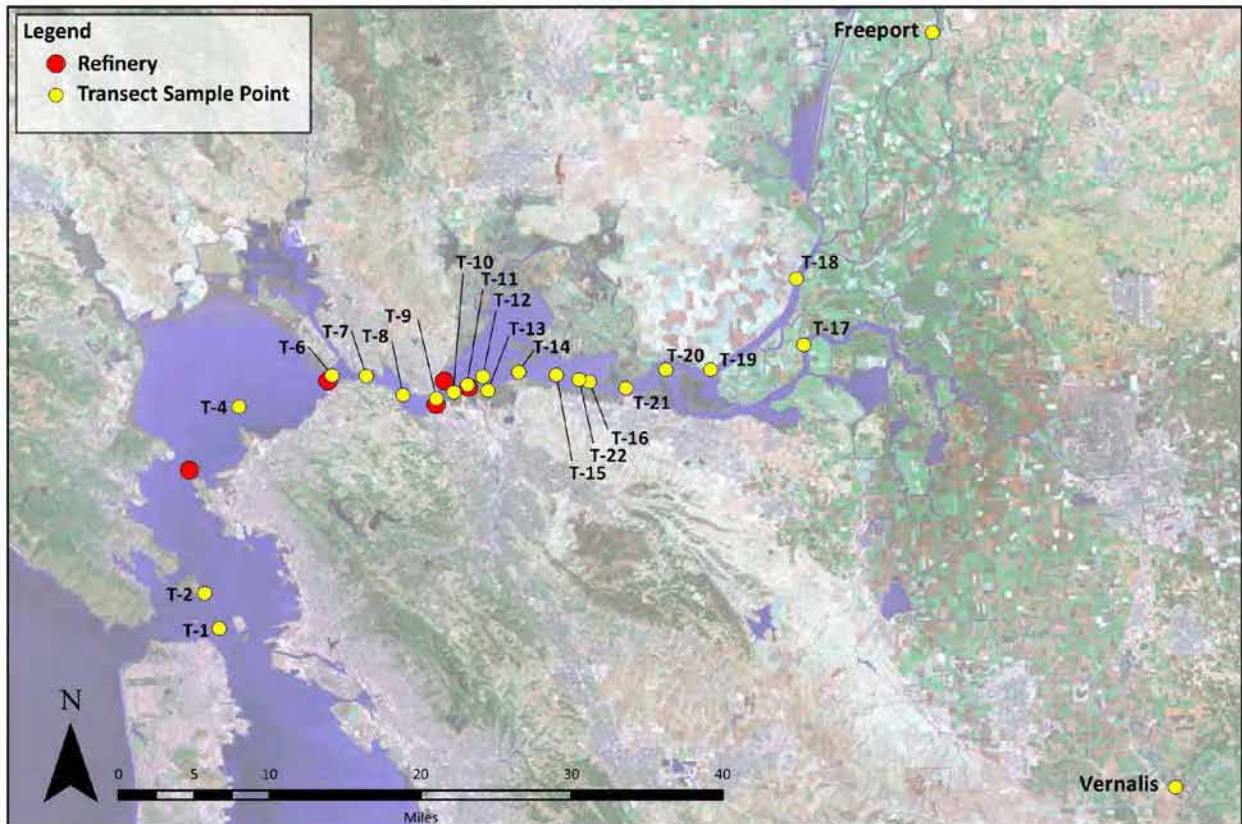


Figure 1 Dry Weather Transect Sample Locations (September 8-9, 2010).

Refinery Effluent – Monthly refinery effluent samples were collected from the fully-treated effluent discharge location. To date, six effluent samples have been collected from the

refineries. The objective of these samples is to characterize each refinery's effluent prior to being diluted by receiving water upon discharge.

Water Quality Sampling Results

Concentrations of different selenium species through the estuary transect are presented in Figure 2 through Figure 7, and discussed individually below.

- Selenite data in the dissolved phase are shown along the estuary in Figure 2 (concentrations in the rivers have not been reported). Concentrations exhibit a slight increase from the freshwater end to Central San Francisco Bay (Central Bay). Concentrations exhibit a greater range in 2010 than in 1999, with concentrations in Suisun Bay lower and concentrations in Central Bay higher than the 1999 values.
- Selenate data in the dissolved phase are shown in Figure 3. For this species, there is a clear difference between the 1999 and 2010 sampling, with concentrations nearly half of their 1999 values at several stations throughout the Bay. Overall, selenate concentrations in 2010 are about twice the selenite concentrations.
- Selenide (organic selenium, or Se(-II)) concentrations are shown in Figure 4 and are considerably variable compared to the selenite and selenate values. The 2010 values are higher than the 1999 values, sometimes by a factor of more than two. The 2010 concentrations exhibit a weak spatial pattern, with a similar range of concentrations across the salinity range. In the 2010 sampling, selenide and selenate concentrations are of similar magnitude (about 0.04 µg/l).

Despite the differences in individual species concentrations in 1999 and 2010, total selenium concentrations (Figure 5) for both periods are quite similar, with slightly higher concentrations in the mid-salinity range, and lower and higher concentrations at the freshwater and seawater ends. The riverine boundary concentrations shown in this figure illustrate the difference between the Sacramento and San Joaquin River inflows. Concentrations in Vernalis are about 7 times greater than at Freeport. Figure 5 also shows the concentrations at the three receiving water stations near each refinery outfall.

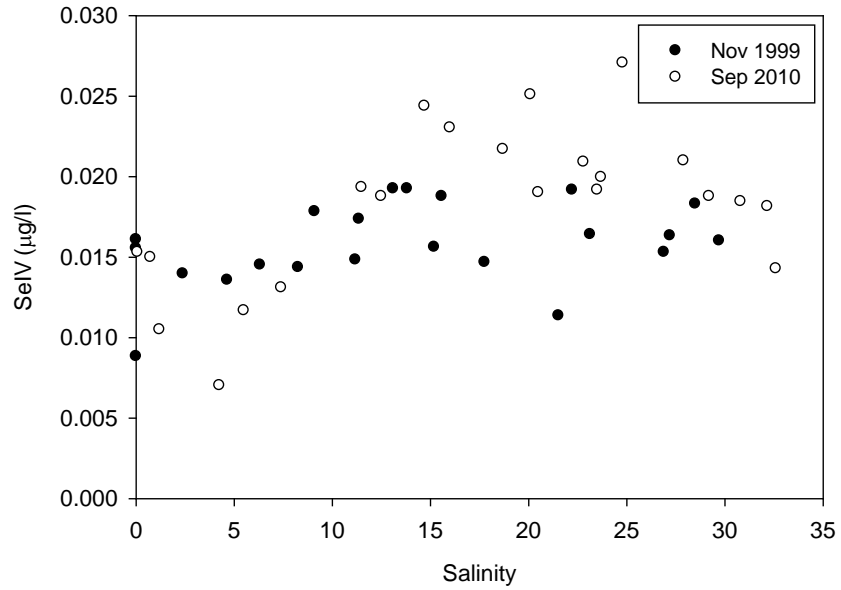


Figure 2 Selenite (SeIV) concentrations across the estuary with data from November 1999 and September 2010.

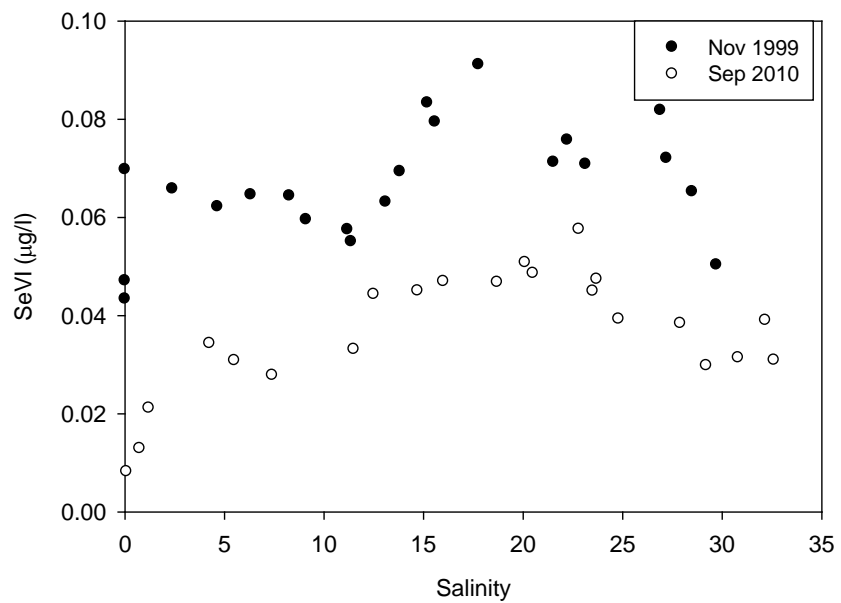


Figure 3 Selenate (SeVI) concentrations across the estuary with data from November 1999 and September 2010.

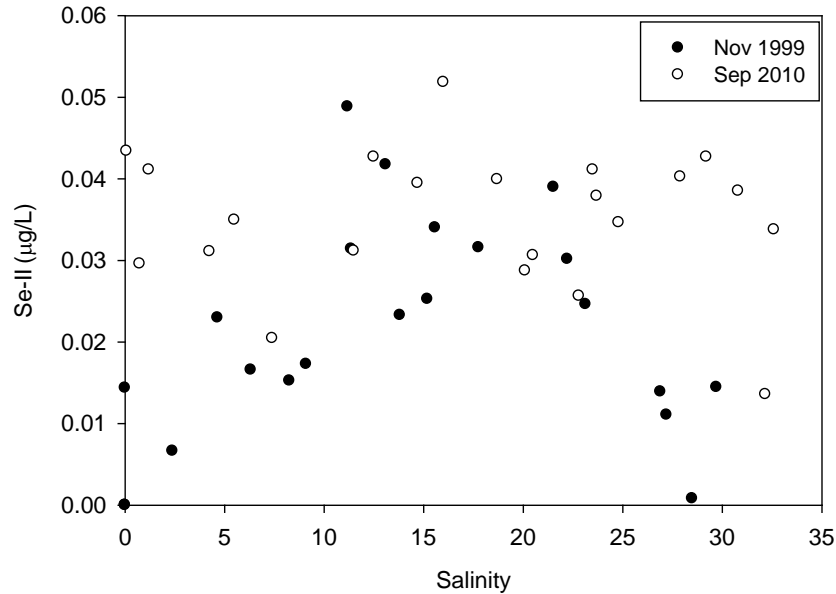


Figure 4 Organic selenium (Se-II) concentrations across the estuary with data from November 1999 and September 2010.

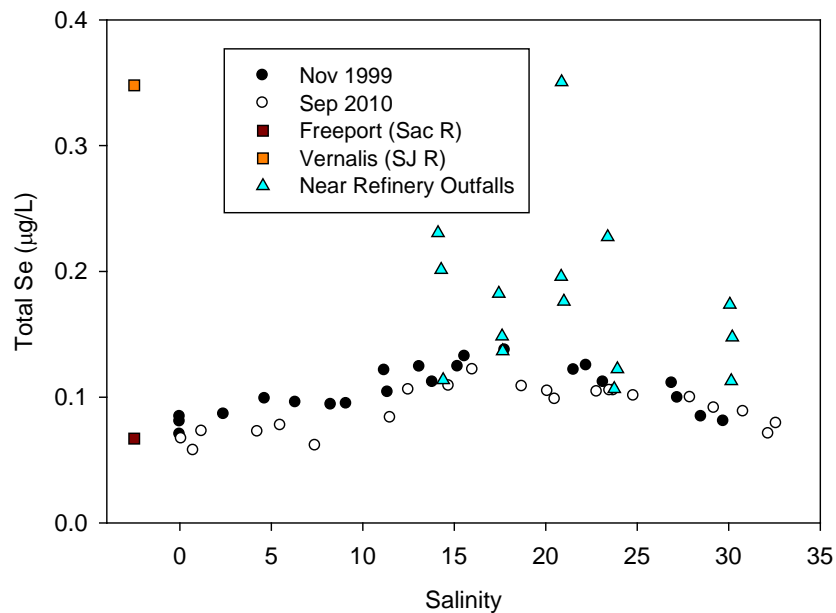


Figure 5 Total dissolved selenium concentrations across the estuary with data from November 1999 and September 2010. Also shown are 2010 data from the riverine sources at Freeport (for Sacramento River upstream of the Delta) and at Vernalis (for San Joaquin River), and stations near the five refinery outfalls

Total particulate selenium concentrations across the estuary (shown as $\mu\text{g/g}$), including the riverine boundary and refinery outfall sites, are shown in Figure 6. Concentrations in the Bay are lower than observed in the riverine inputs for San Joaquin and Sacramento Rivers.

Concentrations in the Sacramento River are approximately half the concentrations in the San Joaquin River. Particulate selenium concentrations in proximity to refinery outfalls are within

the range of the estuary concentrations, unlike the case of dissolved selenium concentrations, where they are noticeably higher than the estuary concentrations.

The ratio of the particulate to dissolved selenium concentrations, expressed as a K_d in units of l/g^1 , across the estuary, including the riverine boundary and refinery outfall sites, are shown in Figure 7. There is significant decrease in the K_d values between 1999 and 2010, which is expected from the preceding plots because the particulate selenium concentrations are lower, even though dissolved selenium concentrations have not changed much over the period of sampling. K_d values are higher in the Sacramento River than San Joaquin River by a factor of about 3, the values at the low salinity end of the estuary are similar to the Sacramento River values. The refinery values are about the same as or slightly lower than the estuary values at nearby locations.

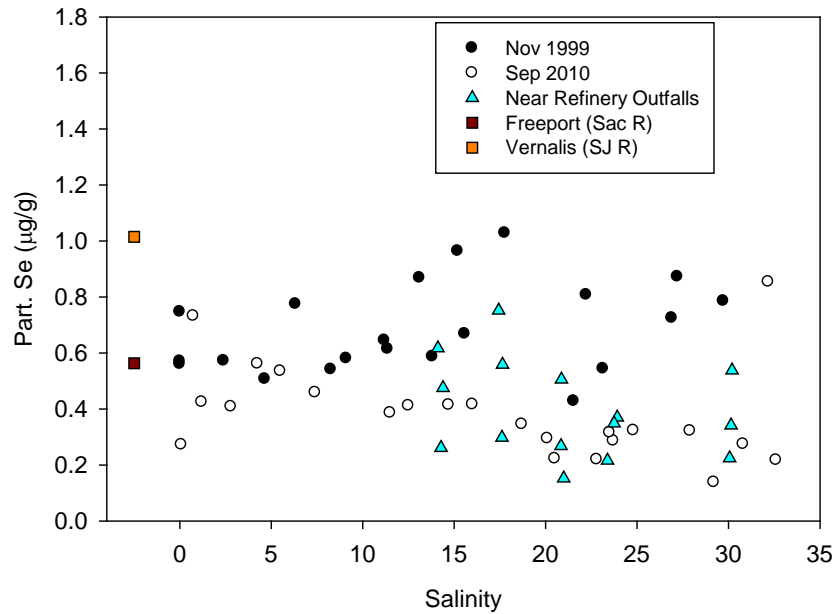


Figure 6 Total particulate selenium concentrations across the estuary with data from November 1999 and September 2010. Also shown are 2010 data from the riverine sources at Freeport (for Sacramento River upstream of the Delta) and at Vernalis (for San Joaquin River), and stations near the five refinery outfalls.

¹ For constituents which can be assumed to be partitioned between the dissolved and particulate phases using an equilibrium-type exchange, K_d is typically termed as the partition coefficient, and is calculated as the ratio of the concentration in the particulate phase to the concentration in the dissolved phase, i.e., $(\mu g/g)/(\mu g/l)$. The final units of K_d are thus l/g . It is also reported in units of ml/g , in which case the numerical values of K_d in Figure 4-12 are multiplied by 1,000. Although the interaction of selenium with particulate materials is not truly an equilibrium-type reaction, the K_d value nonetheless provides an instantaneous snapshot of the ratio between dissolved and particulate phases.

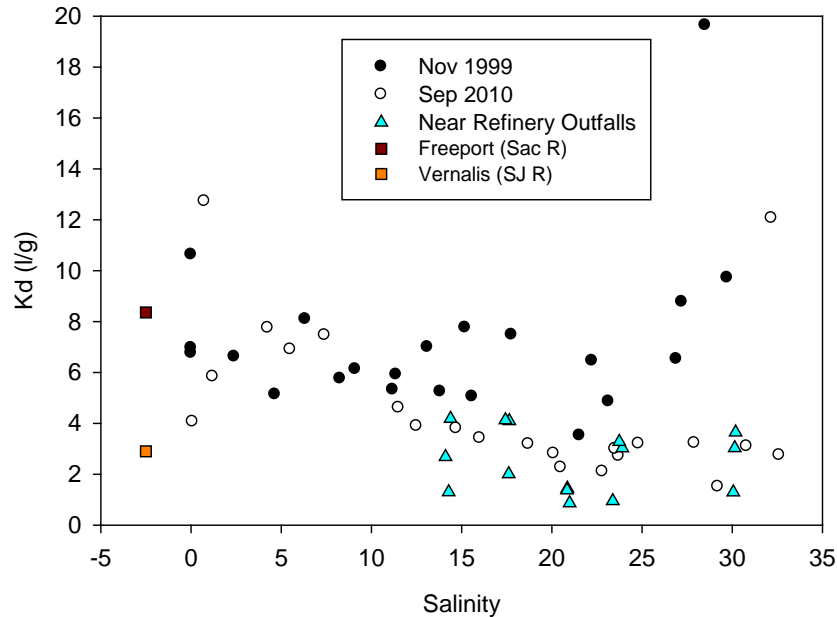


Figure 7 Ratio of particulate to dissolved selenium concentrations (expressed as Kd with units of l/g) across the estuary with data from November 1999 and September 2010. Also shown are 2010 data from the riverine sources at Freeport (for Sacramento River upstream of the Delta) and at Vernalis (for San Joaquin River), and stations near the five refinery outfalls.

Water Quality Preliminary Findings

The discussion presented in this summary report is based on data available to date and is focused on total selenium concentrations in the dissolved and particulate phases, plus speciation in the dissolved phase. Some components of the data that will facilitate interpretation, especially speciation on particulates, are expected to become available soon. However, given the similarity between the last sampling in 1999 and the current sampling, the data obtained in this work can be compared directly with the prior sampling, and allow interpretation of changes over the preceding decade.

The San Joaquin River boundary value of particulate selenium in $\mu\text{g/g}$ is about twice that at Sacramento River at Freeport. The San Joaquin River is widely understood to represent highly contaminated conditions for selenium, and the Sacramento River is thought to represent background conditions. Given this consideration, the range of particulate concentrations is fairly narrow, and because the flow in the Sacramento River is much higher, the role of the Sacramento River needs to be considered in understanding the behavior of selenium in particulates in the system. Compared to the riverine boundary condition (Rio Vista, identified as station T-18 in the 2010 sampling event), particulate concentrations in $\mu\text{g/l}$ at Rio Vista and at Freeport are similar, although concentrations in $\mu\text{g/g}$ are slightly lower at Rio Vista than at Freeport.

Kd values, representing the ratio of particulate to dissolved concentrations, are lower in 2010 than in 1999 by a factor of 2 to 3. This is a significant finding and demonstrates the complexity of selenium uptake by different living and non-living particulate phases. Although a more complete analysis will be performed after the particulate speciation data become available,

these calculations show that any given snapshot of selenium distribution in different compartments should be treated with caution, and that the ratio of particulate to dissolved cannot be assumed to remain fixed over changing conditions, which may include, among other things, changing sources, phytoplankton abundance and species, selenium speciation, and also seasonal and long term hydrological changes.

Overall, these samples provide valuable new information on the state of selenium in the estuary and will continue to form the basis of modeling analysis for the selenium TMDL. Additional data in subsequent phases will allow a more complete interpretation of changes in selenium cycling in the Bay. This set of samples contains the first selenium speciation at the riverine boundaries in the Sacramento and San Joaquin Rivers, which are essential for estimating the external loading to the Bay. Subsequent efforts will also include sample collection in the ocean (using an existing cruise from the University of California at Santa Cruz to obtain samples for selenium analysis), and provide information on the ocean boundary, a data gap that has been identified in previous work.

Discussion of Toxicity Data

With the effort that is underway to develop a water quality criterion based on fish tissue concentration, it is important to take a critical look at the key studies that contribute to the selenium toxicity information in general and the information for species considered for evaluation of selenium exposure risk in the Bay Delta. Much of the freshwater fish literature points to a fairly steep zone in the relationship between tissue concentration and effects usually starting somewhere between 10 and 15 ug/g selenium in which fish go from no apparent effects to effects that may be statistically significant compared to controls but may not be biologically significant.

The interpretation of what tissue concentration results in significant effects --and for that matter a No Observable Effect Concentration, NOEC--is very inconsistent among studies. A review of available fish studies (Table 1) suggests that a selenium concentration > 20-30 ug/g in juvenile or larval fish tissue is probably associated with a biologically significant effect such as an EC20 or EC25 in the better, high quality lab or field studies. Specifically, Table 1 presents a summary of some more recent and relevant tissue-based effects levels for selenium taken from the literature. Notably, studies presenting both no effects levels and lowest effects levels on white sturgeon (Linville 2006 and Tashjian et al. 2006) indicate that effects manifest at tissue concentrations between 12 and 22.5 µg/g. In considering effects to Chinook salmon (*Oncorhynchus tshawytscha*) from selenium, it is useful to consider effects reported for other members of this genus. Rainbow trout (*Oncorhynchus mykiss*) was reported to have an EC15 between 8.8 and 10.5 µg/g. Cutthroat trout (*Oncorhynchus clarkii*) were reported to demonstrate no effects to larvae spawned from eggs with selenium concentrations as high as 21.0 µg/g. Although these values are for egg concentrations, they are substantially higher than the value suggested by USFWS.

Table 1
Summary of Relevant Tissue-based Effects Levels for Selenium

Species	Lifestage	Tissue	Highest Se conc with no effect (ug/g)	Lowest Se conc with significant effect (µg/g)	Reported EC20 or EC25	Source
White sturgeon	Larvae		12	20	21.92	Linville (2006)
White sturgeon	Larvae	Whole Body	14.7	22.5	NA	Tashjian et al (2006)
Bluegill	Juvenile		6.7 – 9.4	10.7 – 16.0	Approx. 15	EPA (2008)
Rainbow trout	Embryo		10	15	25.5	Holm et al (2005)
Bluegill	Larvae		19.5	38.4	23.2	Doroshov et al (1992)
Splittail	Juvenile		10.1	15.1	15.1	Teh et al (2004)
Razorback sucker	Larvae		>12.9	>12.9	>12.9	Hamilton et al (2005)
Chinook salmon	Larvae	Whole body	5.3	10.4	NA	Hamilton et al (1990)
Rainbow trout	Larvae	Egg			~EC15 = 8.8 – 10.5	Holm et al (2005)
Brook trout	Larvae	Egg			~EC15 = 8.8 – 10.5	Holm et al (2005)
Cutthroat trout	Larvae	Egg	20.6	46.8	NA	Rudolph et al (2008)
Cutthroat trout	Larvae	Egg	21.0	NA	NA	Kennedy et al (2000)
Northern pike	Larvae	Egg	8.02	NA	NA	Muscatello and Janz (2009)
White sucker	Larvae	Egg	4.89	NA	NA	Muscatello and Janz (2009)

Toxicity information for two species, white sturgeon (*Acipenser transmontanus*) and Chinook salmon (*Oncorhynchus tshawytscha*) is presented below. Additionally, new information is presented on the potential protective effects of selenium against methylmercury toxicity.

White Sturgeon

The Ph.D thesis by Linville (2006) is often cited as a basis for assessing the effects of selenium on the health and the reproduction of white sturgeon in the Bay Delta, and her work points up several of the technical issues involved in developing a selenium fish tissue criterion. For example, Linville used logit analysis to estimate endpoints for selenium tissue concentrations. With only 3 or 4 treatments, such an analysis has fairly high uncertainty and close inspection of most of the figures presented demonstrate an often non-logarithmic relationship and, in most cases, no apparent relationship between tissue concentrations and effects. This was especially true for the edema effect, an occurrence observed in other studies. Linville does not present

confidence intervals around the logit equations derived and, based on the data given, these would appear to be very large, especially as one goes below the EC50 (which is where the logit analysis might tend to be most accurate). With the data presented, one could as easily conclude that a selenium tissue concentration in juveniles or larvae of about 20 ug/g is an appropriate concentration to use as an EC20 or even NOEC in some cases. Combining experiments as Linville does in Chapter 3 of her thesis is not warranted for several reasons. Linville used two very different types of Se exposures in experiments: one in which larvae were exposed via maternal transfer from adult fish previously exposed to dietary Se over several months; and other experiments in which larvae were exposed to Se via microinjection of selenium. Linville combined the data from these two types of experiments to calculate different endpoints. Using categorized concentrations of Se observed in larvae at the start of larval development from the different experiments, an average percent mortality was estimated, which was biased because the amount of exposure time elapsed at this point in development differed between the two types of exposures. Also, the categories defined by Linville represented ranges of Se concentrations (e.g., 12 – 16 ug/g), which are not supported by the data, given the different Se analysis techniques used in experiments and the fact that these categories were assigned by the author after the fact. Furthermore, the variability surrounding the mean estimates given in these combined analyses were very high (coefficients of variation were conservatively > 40% in most cases due to very few replicates used in different treatments). Combined data were also used by Linville to calculate EC15, EC25, and EC50 based on structural deformities and edema. Again, the variability surrounding each data point in the figures was not presented but is in fact quite high (CVs > 40% for most data points), yielding highly uncertain relationships with Se concentration. Finally, combining results of fish used in all of these experiments increased statistical power of the analysis for some Se concentration ranges (low Se concentrations especially) more than others, which increases the Type I error rate so that an effect is apparently observed but is likely to be a false positive. Of all the experiments presented, the maternal exposure experiment presented in Chapter 3 is the strongest from an ecological perspective because the method of exposure to eggs and larvae is the most realistic. It should be noted that the endpoints calculated by Linville using logit analysis were substantially higher than those obtained using the microinjection technique. While the latter approach does control for some natural variation in transfer of selenium to eggs, it is very invasive and has dubious relationship to real world exposures. While Linville demonstrates that controls responded acceptably to this treatment, larvae were followed for only a few days (to stage 45). It is unclear whether controls would have in fact matured normally over the next several weeks and months. One other point is that Linville does not characterize water quality anywhere in the thesis, except for temperature and dissolved oxygen. There should be data demonstrating the lack of other potential toxicants that would either further stress the organisms or perhaps heighten the effect of selenium in some way.

In summary, the Linville thesis establishes a link between selenium in parental fish tissue being transferred to eggs and larvae and resulting in substantial deformities at concentrations above about 25 ug/g. The issue is that Linville and some others have attempted to identify either effect levels or NOECs that inherently have high variability and are not defensible based on the data reported.

Chinook Salmon

In a recent report (Beckon and Maurer, 2008), the US Fish and Wildlife Service appears to base their analyses and conclusions on a study of dietary selenium exposure to Chinook salmon by

Hamilton et al (1990). Specifically, USFWS used results presented by Hamilton et al. after 90 days of exposure in freshwater as well as following a 10-day brackish water challenge. There were multiple issues with the Hamilton et al. study that have been discussed in the literature (e.g., DeForest et al. 1999). The two primary issues with this study were: 1) the source of the high-selenium feed in one treatment and 2) high control mortality at the 90-day endpoint.

Exposed fish were fed two different diets which included mosquito fish. One diet consisted of fish caught from a reference area that were spiked with seleniomethionine while the other exposure diet included wild-caught mosquito fish from an agricultural drain that was high in selenium (the San Luis Drain or SLD). The SLD fish generally demonstrated greater sublethal (e.g., growth) effects and this may or may not have been related to unknown contaminants present in this diet. USFWS lumped the results from these two different diets together in their analysis as they felt that the tissue-concentration response was similar between the two. The use of the SLD data is inappropriate for use as it was uncontrolled and almost certainly contained contaminants in addition to selenium.

The experiment presented length, weight, and survival data at 30, 60, and 90 days of exposure. There was substantial mortality of control organisms (33.3% in SLD and 27.5% in seleniomethionine) at 90 days in both studies. Conversely, the results at 60 days were quite good (control mortality of 1% in SLD and 0% in the seleniomethionine). USFWS do not appear to have corrected for this increased control mortality when the 90-day data were used.

For the brackish water experiment, USFWS concludes that a tissue concentration of 7.9 µg/g would result in 15% mortality within 10 days (based on USFWS treatment of the Hamilton et al. 10-day brackish water challenge data). The data derived from the SLD diet demonstrates greater resulting tissue concentrations of selenium in the juvenile salmon (28.8 µg/g vs. 23.2 µg/g) than the seleniomethionine diet. However, the seleniomethionine diet resulted in higher mortality than the SLD diet (76% vs. 43%). The interpretation of the Hamilton data by the USGS has several issues as pointed out above. Further, it is not defensible to base a criterion on a 15% effect because this is statistically and ecologically highly uncertain.

Summary of Toxicity Data

The foregoing discussion of white sturgeon and Chinook salmon selenium toxicity studies underscores many of the technical issues and concerns involved in formulating a scientifically defensible tissue-based selenium water quality criterion. A point estimate endpoint related to clear, unambiguous population-level effects due to selenium toxicity is desirable because it inherently establishes an effect level that will sustain sensitive fish populations while not being over-protective to the point that natural variability in selenium tissue levels or fish responses is considered an impairment. An NOEC approach is not desirable because it does not inherently specify an ecologically relevant effect, but rather a statistically significant effect, which may be more associated with experimental design than biology. Two major concerns with the selenium tissue studies for white sturgeon and Chinook salmon are an insufficient range of treatments and effects with which a defensible point estimate can be established, and the use of biological endpoints such as edema frequency, which has been shown to be highly variable and researcher-dependent. Experiments are needed that target several (at least 5) selenium treatments within the range of 0 – 50 µg/g selenium and the endpoint should be based on mortality or structural deformities that are shown to have high reproducibility. The point estimate level needs to take into account natural as well as experimental variability and

therefore should not be based on any effect level less than an EC20. Smaller effect levels are generally not defensible either statistically or ecologically, and an EC20 is typically used when deriving other chronic water quality criteria. In addition, there needs to be consensus on the life stage being targeted for a tissue-based criterion. Different results have been reported in the literature depending on whether tissue concentrations are based on egg, larvae, or juvenile muscle tissue. Much of the recent research has focused on larval selenium concentrations, which appears to be more ecologically relevant than a criterion based on either egg or juvenile selenium measures.

Protective Effects of Selenium

Dietary selenium has been shown to provide protective effects against methylmercury toxicity (Ralston and Raymond, 2010). This research also indicates that selenium is involved in decreasing Hg accumulation in lake fish. There is a high binding affinity between selenium and mercury, and the mercury-selenium complexes formed have low solubility. As a result, the mercury-selenium present in tissues of prey species may not be available for dietary absorption. This relationship between mercury and selenium should be investigated further in the characterization of selenium impacts in the Bay Delta.

Supporting Attachments

Tetra Tech, Inc. 2008. Technical Memorandum #3: North San Francisco Bay Selenium Toxicological Assessment.

Western States Petroleum Association. 2010. North San Francisco Bay Selenium Characterization Study Plan (2010–2012). Submitted to the Regional Water Quality Control Board, San Francisco Bay Region. October 23, 2010.

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2.0 What data, studies, and analytical techniques (for example, models) could be used to improve our understanding of the physical processes, including surface-groundwater interactions, controlling selenium mobilization and transport to and within the Bay Delta Estuary?

A set of analyses in support of the San Francisco Bay Regional Water Quality Control Board's North San Francisco Bay (NSFB) selenium TMDL effort were prepared over 2008–2010. The analyses involved evaluation of the existing scientific literature and existing data in the region, as well as a significant process modeling effort. The analyses are presented in six technical reports. These reports were reviewed by a committee of technical specialists as well as a regional stakeholder group. All reports are in the public domain and available at:

http://www.swrcb.ca.gov/rwqcb2//water_issues/programs/TMDLs/seleniumtmdl.shtml.

The summary below highlights the main findings of the analyses performed in support of the TMDL.

The published literature on the biogeochemistry of selenium emphasizes the role of speciation in biological uptake. The key forms of selenium in the dissolved phase include selenate (Se+VI), selenite (Se+IV), and organic selenides (Se-II). Particulate phase selenium includes elemental selenium (Se0), as well organic selenides in living and non-living material (Se-II), and sorbed forms of inorganic selenium. The pathway of most concern for biological uptake is the conversion of dissolved selenium to particulate forms, its concentration in the tissues of filter-feeding organisms, and its subsequent availability to higher trophic level organisms.

To develop the TMDL, there needs to be a scientifically reliable approach for relating the loads of selenium to concentrations in water, and then relating the water column concentrations to concentrations in the tissues of key organisms that are a focus of the TMDL. A reliable approach must be able to explain the key features of historical selenium behavior, as well as explain the interactions between different species across seasons and years in a dynamic system such as NSFB, where there are consistent seasonal variations in outflow from the Delta, as well as large year-to-year differences in flow. Although simple representations of selenium behavior are possible, including the use of fixed ratios between two compartments of interest, such as a water column:particulate ratio or water column:clam ratio, such methods are not able to explain *a priori* the range of outcomes that have occurred in the recent past or the range of seasonal differences observed today. Most importantly, this approach is unable to explain the seasonal and the inter-annual behavior of *Corbula amurensis* concentrations in the Bay that have been monitored on a continuous basis since 1994. Referring to this issue, the ANPR states the following on page 32: “Recently presented data on concentrations of selenium in North Bay clams, which do not show a clear-cut decline in selenium despite reductions in water column concentrations in San Joaquin River water entering the Bay Delta Estuary, suggest that more information is needed to determine the relationship between river inputs and processes in the downstream environment that affect biotic uptake.”

The information provided in this response and supporting documents provides a process-based explanation for the clam concentration data from 1994-2010. The existence of a framework to explain the observed clam concentrations is important from a long term management

perspective, where many drivers related to selenium uptake may change, such that ratios between compartments (such as water column:particulate ratio or water column:clam) may not be assumed to remain constant. Large scale changes that could be important include changing algal populations and species composition, changes in the food web, and changes in flows through the Delta with the outflow containing a different percentage of San Joaquin River flows than at present.

Evaluation of Selenium Sources

The quantification of selenium loadings from different point and non-point sources including Sacramento River and San Joaquin River inputs through Delta, local refineries, POTWs, tributaries and sediments, during both dry and wet seasons, was the first component of this analysis (See attached document: *Technical Memorandum 2 North San Francisco Bay Selenium Data Summary and Source Analysis*). Although selenium speciation in the Bay is not monitored in a systematic manner, there are several ongoing programs in the region that monitor some form of selenium (typically total dissolved selenium) at selected locations. These data were the basis of the load estimates developed in the aforementioned document.

The analysis of sources indicated that the annual loadings from the Central Valley through the Delta are the largest source of selenium with high variability depending on total flow through the Delta. Loads in high flow years are estimated to be more than ten times higher than in low flow years. The average Delta load is estimated to be 3,962 kg/yr. Local tributaries draining both urban and non-urban areas, although contributing lower flows than the Sacramento and San Joaquin Rivers, have high selenium concentrations, and are also a large source of selenium during the wet months (estimated average load of 354-834 kg/yr). Refineries are estimated to contribute ~550 kg/yr to NSFB, although these loads were higher prior to the late 1990s when wastewater controls were installed. The point source loads (the refineries and the POTWs) contribute relatively uniform loads over the year, although the non-point source loads (the Delta and the local tributaries) contribute substantially more load in the wet season than in the dry season.

Model Framework

The fate, transport, and biological uptake of selenium in the Bay-Delta system are influenced by intra- and inter-annual flow variability, and selenium transformations among different dissolved and particulate forms. To represent these processes, an estuary model was used to simulate the selenium concentrations in the water column and bioaccumulation of selenium in the NSFB (ECoS3 model, Harris and Gorley, 2003). The model built upon the previous work of Meseck and Cutter (2006) and was applied in one-dimensional form to simulate several constituents including salinity, total suspended material (TSM), phytoplankton, dissolved and particulate selenium, and selenium concentrations in bivalves and higher trophic organisms.

Selenium species simulated by the model include selenite, selenate, and organic selenide. The particulate species simulated by the model include particulate organic selenium, particulate elemental selenium, and particulate adsorbed selenite and selenate. The uptake of dissolved selenium by phytoplankton includes uptake of three species (selenite, organic selenide and selenate). The interactions between these species are represented as first-order reactions, with rate coefficients estimated through calibration in NSFB (Figure 8). Bioaccumulation of

particulate selenium to the bivalves was simulated using a dynamic bioaccumulation model (DYMBAM, Presser and Luoma, 2006), applied in a steady state mode. Bioaccumulation into bivalves considers the different efficiencies of absorption for different selenium species (Figure 9). Bioaccumulation to higher trophic levels of fish and diving ducks is simulated using previously derived linear regression equations by Presser and Luoma (2006), and estimates of trophic transfer factors summarized from the literature (Presser and Luoma, 2009).

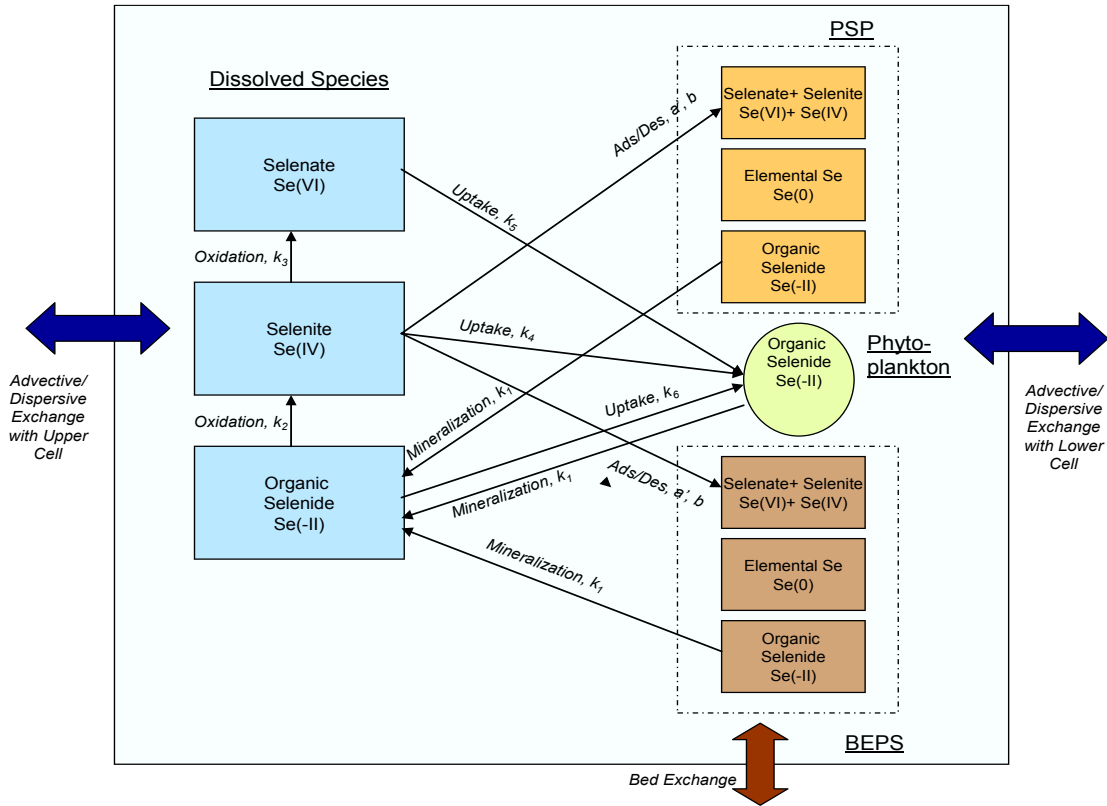


Figure 8 Representation of selenium exchanges between different compartments in each cell of the model. Transformations are shown for each species in the dissolved and particulate phases (PSP, permanently suspended particulates; phytoplankton; and BEPS, bed exchangeable particles). Bivalves consume particulate selenium that is a mix of PSP, BEPS, and phytoplankton.

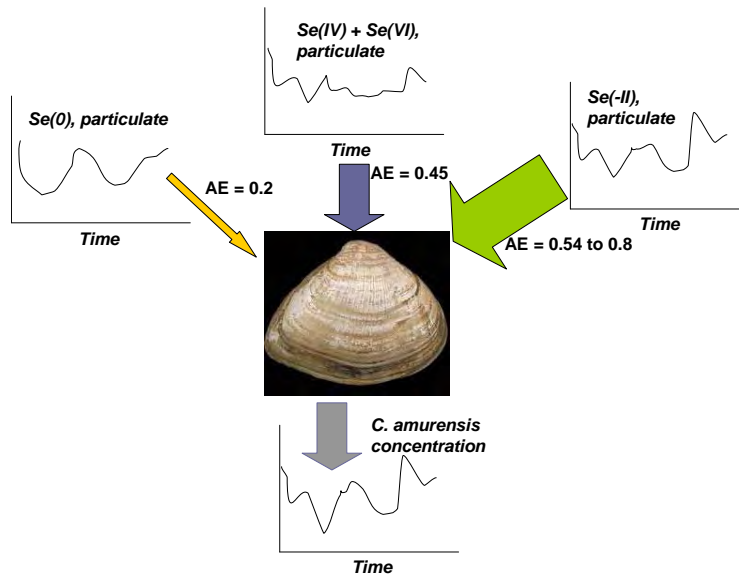


Figure 9 Representation of uptake by clams. The assimilative efficiency (or AE) is a function of the form of the particulate selenium. The highest AE is for organic selenium (Se-II), as would be associated with living and non-living material, and the lowest if for elemental selenium (Se (0)). See Tetra Tech (2010) for detailed literature references for these AE values.

Detailed information on model development, calibration, evaluation, sensitivity evaluation and application to future scenarios is presented in attached document titled *TM-6: Application of ECOS3 for Simulation of Selenium Fate and Transport in North San Francisco Bay*. The model encapsulates a great deal of information about the behavior of NSFB, relating to constituents that influence selenium, such as flows and salinity, suspended particulates, and phytoplankton abundance. These ancillary constituents, unlike selenium speciation, are monitored consistently throughout the Bay by the US Geological Survey (USGS). Important model inputs for which data were available over a simulation period of 1999-2006, include flows in the rivers and local tributaries, chlorophyll a concentrations, suspended solids concentrations, salinity, and total selenium in the rivers and point sources. Data on selenium speciation (in the dissolved phase and in the particulate phase) on selected loads (refineries and riverine sources) were available primarily for 1999 at time of model development. It is important that the model be updated with the new data being collected over 2010-2012, and described in response to Question 1 of the ANPR, and presented in Figures 2 through 7.

Key Features of Bay Conditions

The distribution of selenium across the Bay is discussed in the context of the model calculations. Loads in NSFB are described for 1999, a year for which there are data from a variety of sources, and which is representative of current levels of point source loading. Estimated loads are shown for total selenium as well as for particulate selenium for 1999 in Figure 10. As noted above, non-point sources constitute a large fraction of the external total selenium loads, and are the primary external source of particulate selenium loads. These loads vary by season and by year driven largely by variations in flow in the principal rivers (Sacramento and San Joaquin) and local Bay tributaries.

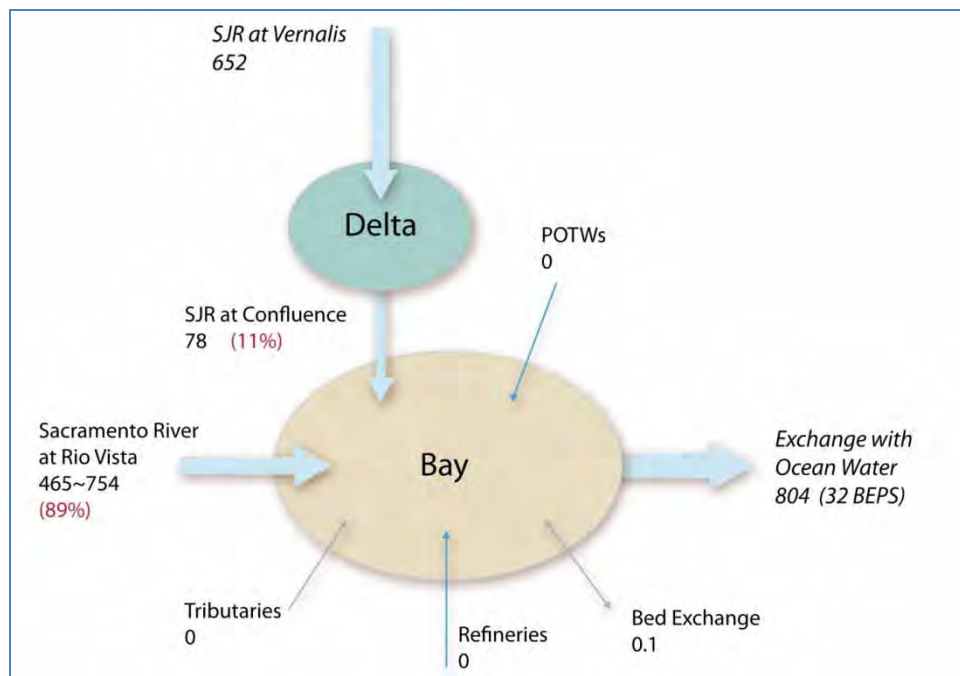
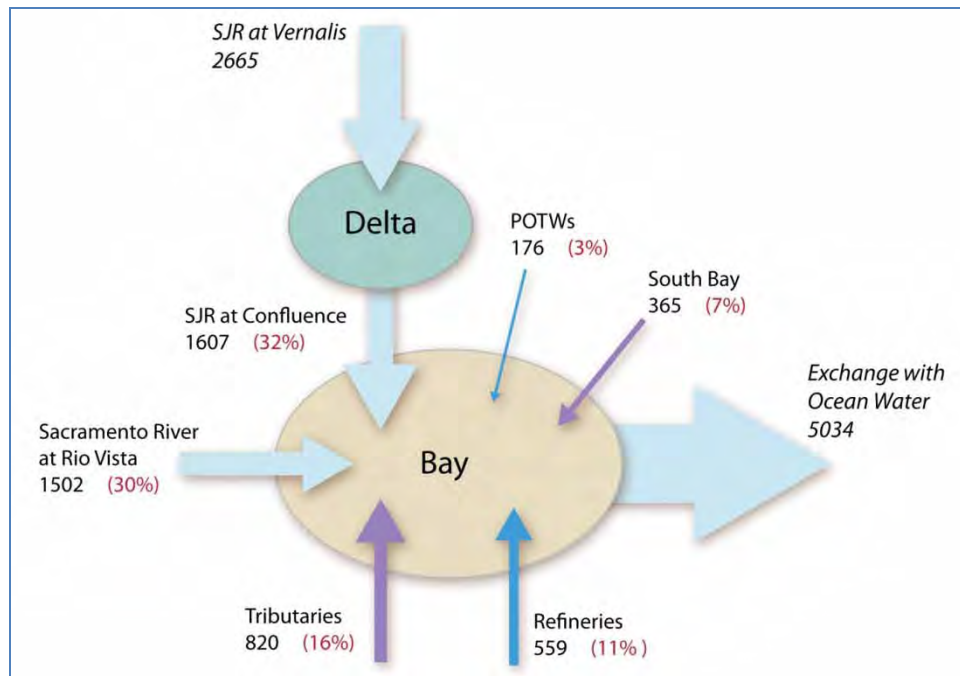


Figure 10 Loads of selenium in San Francisco Bay in kg for 1999: total selenium (upper panel) and particulate selenium (lower panel).

Also important to consider is the variation in total suspended material (TSM) in the Bay water column between the wet and dry seasons. TSM includes mineral rich particles as well as particles of biological origin, such as living and non-living phytoplankton. Values of TSM are shown in Figure 11 for a wet weather day and for a dry weather day in 1999. On the dry weather day, the concentration of TSM from the Delta is relatively high (40 mg/l), but decreases rapidly

through Suisun Bay and Carquinez Strait to 10 mg/l. In contrast, on a wet weather day in the same year, the outflow concentration from the Delta is similar (45 mg/l), but the concentrations in Carquinez Strait are much higher (62 mg/l). The difference is caused by the higher outflow volumes from the Delta on the wet weather day, with high sediment concentrations. Using data such as these, the behavior of suspended material in the Bay can be conceptualized as shown in Figure 12 . The suspended material originating in the riverine sources, which is higher in mineral content, tends to settle as the flows enter the Bay. The contribution of the in situ generated particles, primarily phytoplankton, increases as a share of the total particulate load as one travels from the riverine to the ocean end.

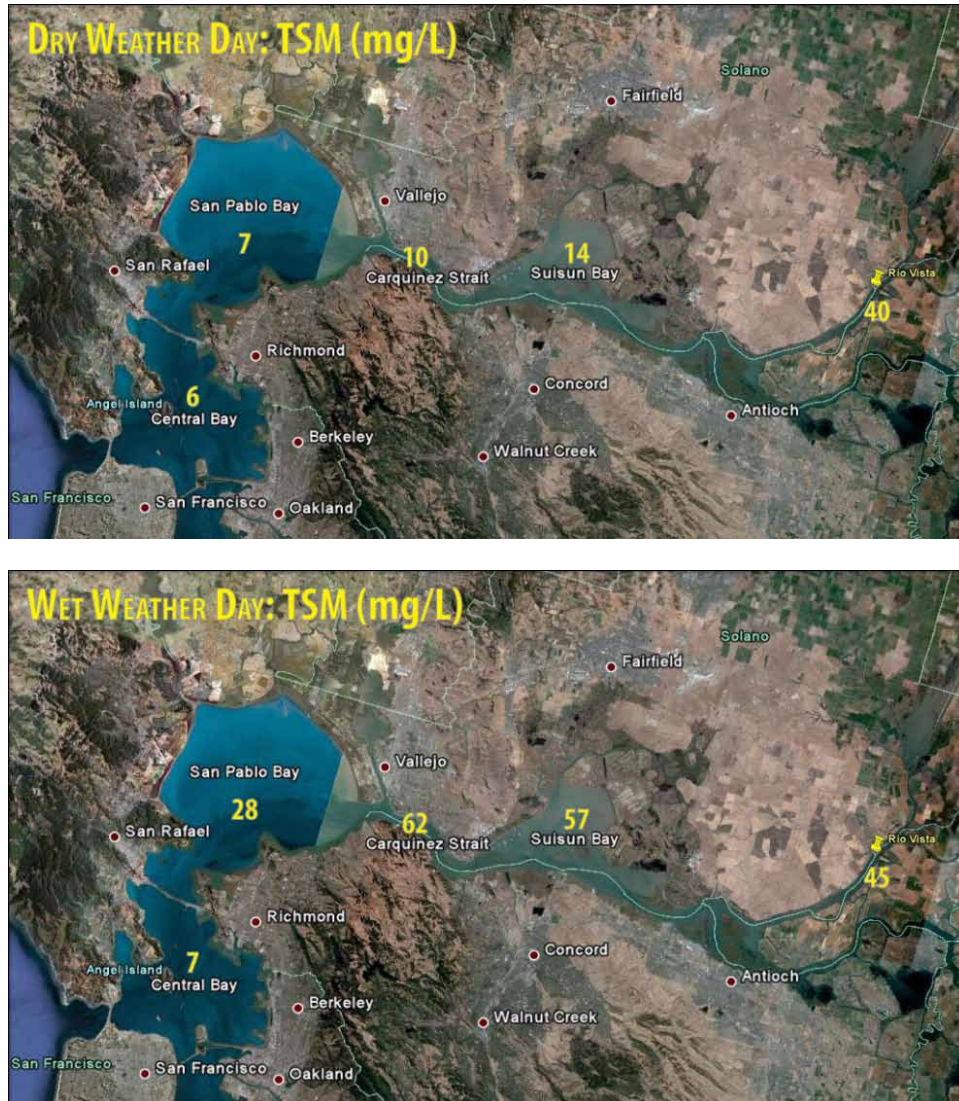


Figure 11 Modeled total suspended material (TSM) from Rio Vista to Golden Gate for a dry weather day and a wet weather day for an average flow year (1999).

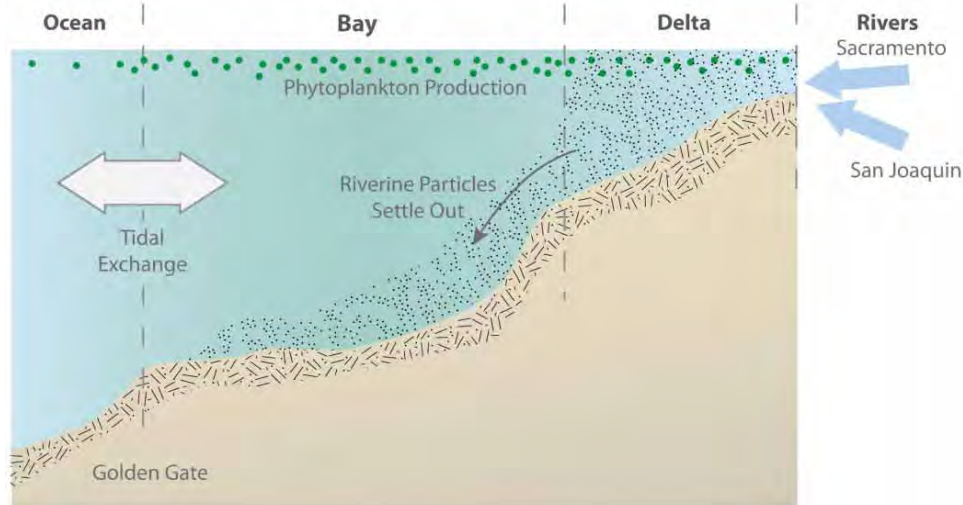


Figure 12 Behavior of suspended particulates in the Delta and Bay.

The overall behavior of particulates also influences the distribution of particulate selenium in the Bay as shown in Figure 13. In this figure, the mix of particulate selenium forms (organic, inorganic, and elemental) is shown across the estuary for the same dry and wet weather days that were used in Figure 11. In both cases, the fraction of organic selenium increases from the riverine to the oceanic boundary, driven by the settling of mineral particles and the increasing relative share of organic particles. In the dry season, especially in Suisun Bay, Carquinez Strait, and San Pablo Bay, the fraction of organic selenium is higher. As shown in Figure 9, the higher organic fraction is indicative of greater assimilative efficiency by clams.

Finally, the ratio of dissolved and particulate selenium can also be examined over time and across the estuary. The changing mix of suspended particles, i.e., mineral versus organic particles, also affects the concentration of selenium expressed as $\mu\text{g/g}$ because the organic fractions, especially algal cells can be richer in selenium. Thus, the ratio of particulate to dissolved concentrations (termed K_d , as discussed in the response to Question 1) increases as the organic fraction of the suspended particles increases. This is shown in Figure 14 where the K_d values are shown for a dry weather and a wet weather day in 1999. The K_d values increase from the riverine to the oceanic end, and are higher in the dry season when the mineral component of the particulates are lower.

Even as the significant changes in the particulate selenium speciation and K_d occur in space and across seasons, the dissolved concentrations vary over a narrow range in both the dry and wet weather days: 0.07 to 0.088 $\mu\text{g/l}$ and 0.077 to 0.103 $\mu\text{g/l}$ respectively (values shown in Figure 14). The role of the distribution of particulates is shown in conceptual form in Figure 15. In the dry season, the contribution of riverine particulate selenium is small relative to the in situ generation of phytoplankton. These conditions also result in higher particulate selenium concentrations (in $\mu\text{g/g}$). In the wet season, the contribution of riverine particulates is larger relative to in situ generation, and the overall particulate composition is more mineral and lower in selenium concentration. Of course, the riverine contributions of particulate selenium change from year to year, with resulting consequences on concentrations in the Bay.

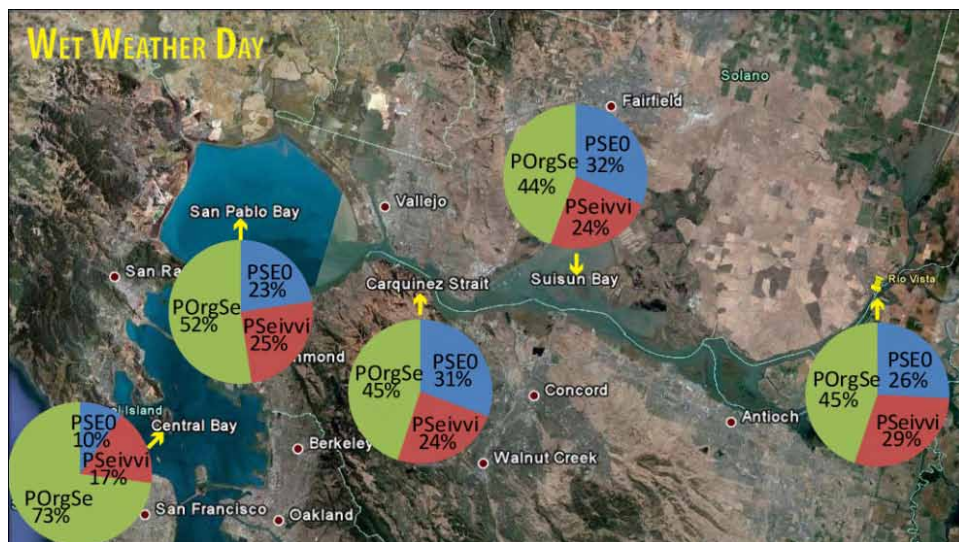
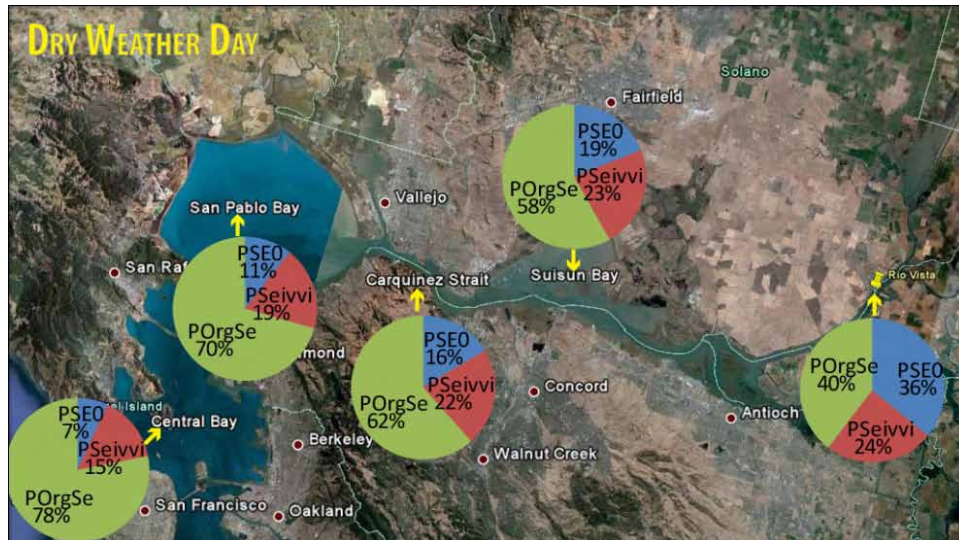


Figure 13 Modeled particulate selenium (PSEO = elemental selenium; PSeivvi = inorganic selenium; POrgSe = organic selenium) from Rio Vista to Golden Gate for a dry weather day and a wet weather day for an average flow year (1999).



Figure 14 Modeled K_d and particulate and dissolved selenium from Rio Vista to Golden Gate for a dry weather day and a wet weather day for an average flow year (1999).

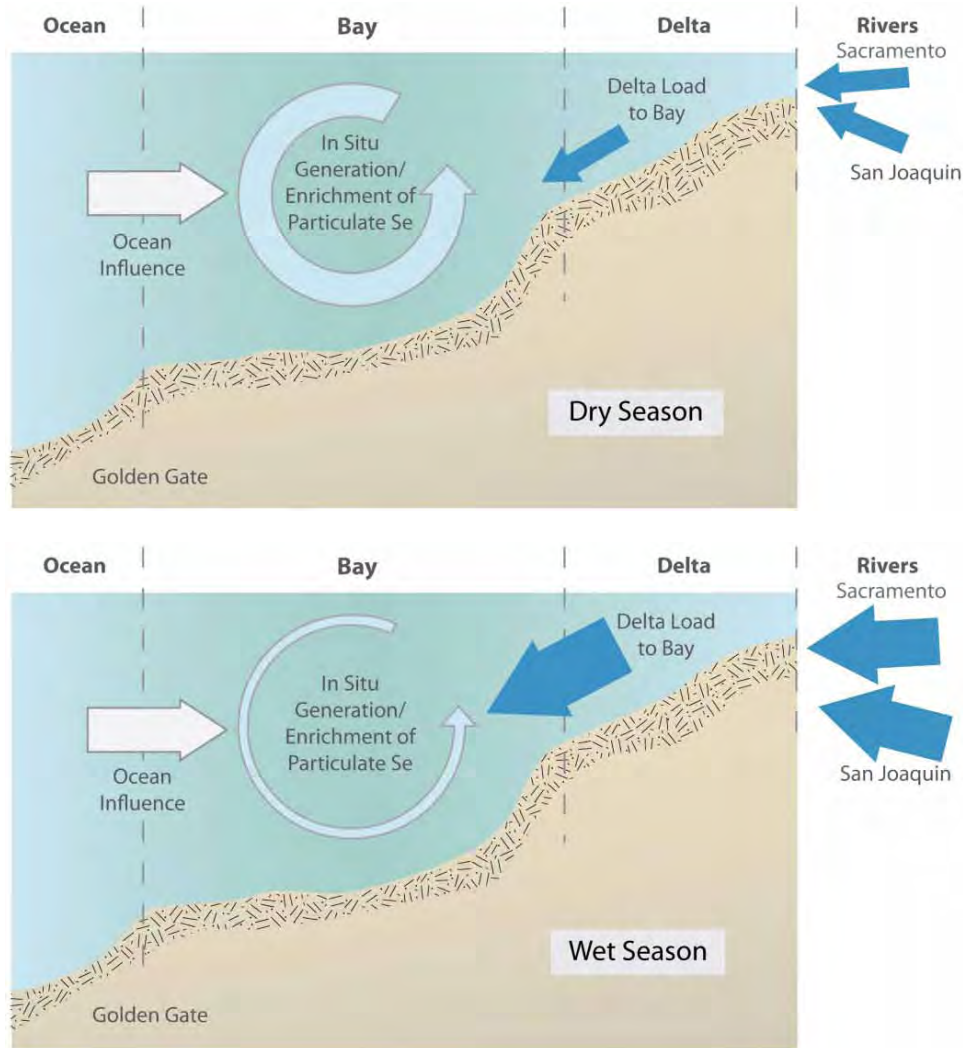


Figure 15 Cycling of particulate selenium in the dry season (upper panel) and the wet season (lower panel).

Ability to Explain Selenium Behavior in the Estuary

The above summary of selenium cycling, embodied in the NSFB selenium model is best illustrated by the use of the model for explaining the 15-year clam data set in the Bay (Kleckner et al., 2010), representing a period with changing hydrology and loads, particularly decreases in refinery wastewater loading beginning in 1998, and a general reduction in San Joaquin River loads through selenium source control actions in the San Joaquin River watershed. Over this period of record, two features stand out in the clam data: there has not been a large reduction in clam concentrations despite the load changes, and there is a significant amount of inter-seasonal variability, with the lowest concentrations in each year occurring during the high flow months, and the highest concentrations occurring in the low flow months. Seasonal high concentrations are almost a factor of two as high as the low concentrations. The seasonal pattern in clams is a feature of the data that cannot be explained by the dissolved selenium concentration data alone, as the dissolved data do not show a similar seasonal pattern.

The NSFB selenium model was applied using measured riverine inflows, as well as using the calibrated parameters for selenium transformation based on the 1999 speciation data, and uptake rates and assimilation efficiencies for different selenium species. A reduction in point source loads, through improved refinery wastewater treatment, is also included in the model inputs. The resulting calculation is shown in Figure 16 and compared against the observed data. The model is able to capture key features of the data very well, including seasonal and inter-annual variations. Changes in clam selenium concentrations from one year to the next are influenced significantly by hydrology, with wet years (such as 2005 and 2006) resulting in lower clam concentrations. The ability to explain this temporal clam behavior is important in itself and also provides insight into future changes in the Bay, where flow modifications in the San Joaquin River or the Delta may result in riverine inputs that differ from historical, both in volume and in the amount of particulate selenium represented by the relative proportion of Sacramento and San Joaquin River flows.

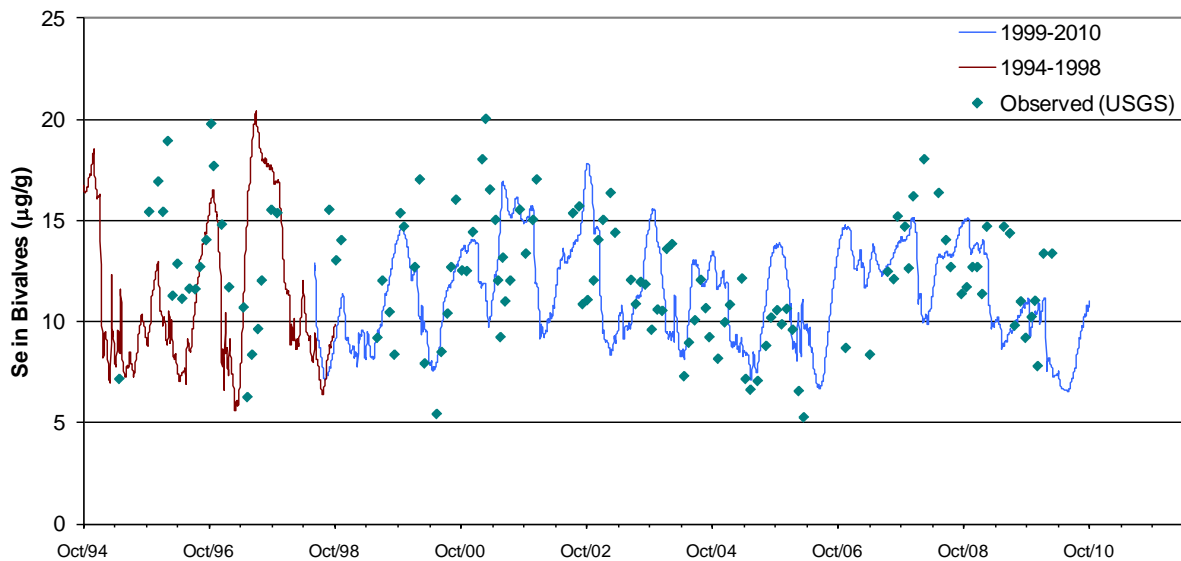


Figure 16 Simulated selenium concentrations in bivalve *Corbula amurensis* compared to long-term data from USGS at the Carquinez Strait for the period of 1994-2010 (Kleckner et al. 2010). Flow data used: DAYFLOW records; Refinery data used: daily data for 1999-2007, constant loads after 2007; San Joaquin River Selenium: observed data at Vernalis, multiplied by Delta removal constants with fixed speciation: SeIV: 0.028; Se VI: 0.658; OrgSe: 0.314.

Why a Complex Model is Needed

The model computations of dissolved and particulate selenium could be compared with a somewhat simpler published approach based on linear partitioning between dissolved and particulate phases (Presser and Luoma, 2006, 2010). The Presser and Luoma approach is easy to explain to stakeholders and is relatively transparent, which are clearly valuable assets in a TMDL-setting process. However, the model does not fully capture the processes associated with particulate selenium uptake and transport, which influence the results obtained for load changes from the current situation. In the linear partitioning approach a reduction in dissolved concentrations results in a proportional reduction in particulate concentrations, a result that is

different from the ECoS dynamic uptake/mineralization approach and consideration of external particulate sources. In particular the more complex approach illustrates that there is a floor in particulate concentrations set by the Sacramento River outflows, and that changes to dissolved concentrations alone, such as through the controllable sources in the Bay and San Joaquin River watershed will not achieve a bay-wide reduction in particulate selenium below the floor set by the Sacramento River.

The ability to explain the clam data presented above is a key advantage of the use of a more process oriented model that can be applied in settings where there are many changing factors, and where the assumption of a constant K_d ratio is not valid. In this specific case, for example, there is a systematic two-fold increase in clam selenium concentrations from the wet to the dry seasons each year, that is not related to the dissolved phase concentrations which are relatively uniform. A process-based explanation using the contribution of riverine particulates to the Bay provides a reasonable explanation, and can capture the essence of the changes over time.

Selenium issues in the Bay have been studied for nearly three decades, and management of selenium will be a long term effort, during which many changes in the Bay-Delta system can be expected. To best address these future conditions, it is important to develop tools, such as the one presented here, to capture the greatest amount of process detail that is possible. The application of a process-based model does not completely reduce the uncertainty associated with future projections, but it does provide a robust scientific basis upon which projections can be made.

Supporting Attachments

Tetra Tech, Inc. 2008. Technical Memorandum #2: North San Francisco Bay Selenium Data Summary and Source Analysis.

Tetra Tech. 2010. Technical Memorandum 6: Application of ECoS3 for the Simulation of Selenium Fate and Transport in North San Francisco Bay.

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3.0 What data are needed to track selenium impacts in the Bay Delta ecosystem as currently configured, and to evaluate potential impacts of selenium under changed flow and transport conditions into and within the Delta?

In the ANPR discussion of water quality standards in the Bay Delta Estuary related to selenium, it is noted that the efforts underway will use data on affected species. The Presser-Luoma ecosystem-based model that accounts for food web processes and site-specific conditions is also identified as a tool that will be used in this effort. Although a variety of data from field sampling exists that have been used to either evaluate the existence of environmental impairment or that have already served as a basis of parameterizing the Presser-Luoma model, there is a need to develop a focused monitoring approach to develop information that can be used to establish existing conditions in the Bay Delta with respect to the effects of selenium. This information will also serve as a basis for measuring change to the system and to gauge the effects of ecological forcing factors such as changes in food-web structure, flow conditions, and differences sources and forms of selenium to the system. While there have been several efforts to develop conceptual models of selenium behavior in the Bay Delta Estuary (ref), numerous gaps exist in either the knowledge of the relative importance of identified factors or in the completeness of the data that can be used to model the ecosystem. The risks of having insufficient data to conduct the planned modeling and analyses include the selection of values from sparse or incomplete data sets that support the existing concepts regarding both the relative importance of factors that affect the system and the existence of impairment.

The data needs are best classified into the following sections, each of which is described below: Delta selenium concentrations, *Corbula amurensis* selenium concentrations and abundance, ocean boundary conditions, higher trophic level organism data, and a sustained selenium modeling effort.

Delta selenium concentrations. The Bay currently receives its largest selenium load from the Delta, which reflects the mixing of the Sacramento and San Joaquin Rivers, the export of a significant fraction of selenium through the aqueducts, and the transformation and uptake of selenium in the Delta. However, the behavior of selenium in the Delta has been inadequately monitored, and the process-level understanding is limited. To be specific, there are very few measurements of selenium within the Delta, and aqueduct exports are poorly characterized because the detection limits are too high. None of the routine monitoring, including at the major riverine inflows at Freeport (on Sacramento River) and Vernalis (on San Joaquin River) consists of any speciation of selenium, including a basic separation into dissolved and particulate selenium. An understanding of selenium through this region is all the more important because there is a possibility that the Delta may be reconfigured to deliver more Sacramento River water to the aqueducts, in effect increasing the supply of San Joaquin River to the Bay. San Joaquin River selenium concentrations are roughly 10 times higher than the Sacramento River, and the modeling presented in Tetra Tech (2010) indicates substantially increased concentrations in the Bay if a greater fraction of Delta outflow were to be comprised of San Joaquin outflow. For this reason, a regular monitoring program that includes selenium speciation through a network of stations in the Delta is important to implement.

Corbula amurensis selenium concentrations. The elevated risk of selenium to benthic feeding organisms is strongly tied to efficient uptake by the invasive clam, *Corbula amurensis*. Concentrations in this clam provide a useful indicator of selenium in Bay particulates, and it is important that this monitoring be continued in the foreseeable future. At present, these data are not routinely released to the public, and the 1995-2010 were only recently released (Kleckner et al., 2010). Easier access to these data, perhaps on an annual basis would make these more useful to the Bay scientific community and allow interpretation of the influences of selenium loads and hydrology on possible uptake.

Corbula amurensis abundance. The clam *Corbula amurensis* is thought to be an important part of the diet of benthic-feeding organisms. However, there is little publicly reported information on its abundance over time. A program, perhaps tied to the existing clam selenium monitoring program, that also reports the abundance of these organisms in units of biomass per unit area, would provide valuable information on the potential contribution to the diet.

Ocean boundary conditions. Besides the Delta, another important source of relevance to particulate selenium in the Bay is concentrations in the Pacific Ocean beyond the Golden Gate Bridge. Although the suspended material concentrations in the ocean are lower than in the estuary, particulate selenium concentrations (measured as $\mu\text{g/g}$) may not follow the same pattern. Measurement of ocean particulate selenium values is part of the 2010-2012 sampling plan, but longer term monitoring of this boundary is also recommended.

Higher tropic level organism monitoring data. There are existing monitoring efforts to determine fish and bird egg concentrations of selenium, conducted by different agencies around NSFB, although it is not clear if these are part of a formal monitoring program. The data are also not readily available. There needs to be an effort to coordinate the existing programs and perhaps make the information available in a central repository, along with information relating to clams and water quality.

One of the key indicators of impairment due to selenium in the Bay-Delta is the concentration of selenium in the muscle tissue and/or liver of the white sturgeon (Linville, 2006). While, as noted in the response to Question 1, there is uncertainty regarding the toxicity endpoint, the information on the concentrations of selenium in white sturgeon is incomplete. Based on the review of existing information, over a period of 13 years (1997 – 2009) 122 measurements of selenium in the muscle tissue of white sturgeon have been made (Table 2). The average concentration of selenium in the fish-tissue samples exhibit a relatively small range (4.3 to 10.4 mg/g-dw) over the Bay Delta, and the coefficient of variation (a gauge of sample-value variability, standard deviation/mean) is relatively small for environmental sample. However, given the differences in the size of the fish included in the different samples and the small sample size there is insufficient data to evaluate either the existence of impairment or the evaluation of trends.

With the planned use of the Presser-Luoma ecosystem model for deriving a water quality criterion for selenium in the Bay Delta, data on the diets of the fish such as the white sturgeon will be important in developing field-derived trophic transfer factors. For example, with the apparent enhanced selenium bioaccumulation ability of the clam *Corbula amurensis* it is necessary to quantify the importance of this species to the mixed diet of the white sturgeon. The existing information on the relative importance of all molluscs in the diet of white sturgeon

was summarized by Beckon and Maurer (2008) and is summarized in Table 3. These data indicate that molluscs can be a significant but highly variable contribution (generally below 50%) to the mixed proportion of the prey of white sturgeon. However, with the increase in the population of *C. amurensis* in the Bay Delta there is a concern that a dietary shift and an increase in the importance of this prey item of white sturgeon will lead to an increase in the bioaccumulation of selenium in the white sturgeon. For example, citing Feyrer et al (2003), Stewart et al (2004) note that since the introduction in 1986, *C. amurensis* has been a dominant food item in the digestive tracts of benthivorous sturgeon. However, while Feyrer et al (2003) reported on changes in the diets of 12 species of fish in Suisun Marsh, they did not present any data for the dietary preferences of the white sturgeon. New data on the importance of *C. amurensis* in the diet of white sturgeon as well as the abundance of the clam population is needed in the assessment of selenium impacts in the Bay Delta ecosystem.

Ongoing selenium modeling support. Over time, selenium transport cycling in the Bay is expected to change, driven by hydrologic variability, Delta modifications, land use changes in the watershed, changing algal species and abundance, and possible changes in the distribution of organisms in the Bay. Sustained support of a modeling framework that ties together these elements and can be tested against the data should be an important component of the overall monitoring strategy for the Bay.

Table 2
Summary of available measurements of Se in the muscle tissue of white sturgeon.

Location	Year	Sample Size	Avg. Fish Muscle Tissue Concentration µg/g-dw	C.V. (%)	Fish Length (cm.)	
					Min.	Max.
San Pablo Bay	1997	7	6.3	74	117	145
	2000	6	8.3	41	115	149
	2002	3	8.9	37	91	126
	2003	2	4.3	20	122	137
	2004	14	8.0	36	128	171
	2006	6	5.8	50	-	-
	2009	6	8.7	57	-	-
North Bay	2003	20	4.9	30	61	110
	2004	2	10.4	16	126	150
South Bay	1997	6	4.6	46	117	149
	2000	4	6.7	22	121	182
	2003	5	8.0	59	117	163
	2009	7	4.6	33	-	-
Baywide	2000	15	9.2	76	123	171
	2001	17	10.1	48	127	158

Table 3
Percent frequency of occurrence of molluscs in esophageal and stomachs of white sturgeon
(sample size). Data from Tables 8 -10 Beckon and Maurer (2008)

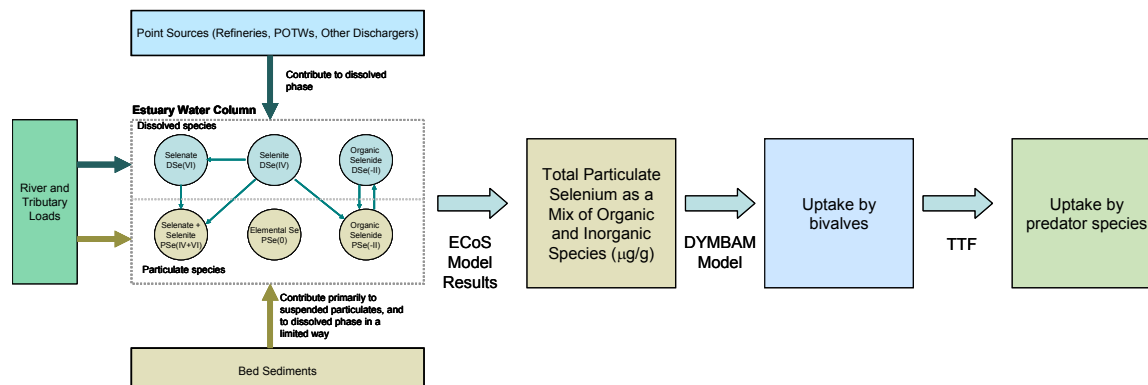
	Fall	Winter	Spring	Summer
Suisun Bay and Carquinez Strait, 1965 - 1967	77 (41)	44.9 (15)	21.1 (59)	40.7 (27)
San Pablo Bay, 1965 - 1967	33.0 (39)	14.9 (49)	14.7 (99)	42.2 (35)
Sacramento-San Joaquin Delta, 1963 1964	0.1 (42)	< 0.1 (13)	< 0.1 (27)	< 0.1 (23)

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TECHNICAL MEMORANDUM 6: APPLICATION OF ECoS3 FOR SIMULATION OF SELENIUM FATE AND TRANSPORT IN NORTH SAN FRANCISCO BAY

Final Report, February 2010



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This Technical Memorandum has undergone a scientific review by the Technical Review Committee, and we thank the reviewers for their contribution to the preparation of this report.

Technical Review Committee members:

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- Dr. Regina G. Linville, California State Office of Environmental Health Hazard Assessment
- Dr. Samuel N. Luoma, Emeritus, U.S. Geological Survey
- Dr. John J. Oram, San Francisco Estuary Institute

The role of the Technical Review Committee was to provide expert reviews of the modeling process as well as credible technical advice on specific issues arising from the review process. Appendix 5 provides a record of the technical review process, presents the comments of the Technical Review Committee members, and identifies the actions that were taken in response to the Technical Review Committee's comments.

We would like to thank Shannon Meseck (National Marine Fisheries Service) and Gregory Cutter (Old Dominion University) for providing the code for an earlier version of the model and for providing selenium data in San Francisco Bay. We would also like to thank John Harris (formerly of the Plymouth Marine Laboratory, United Kingdom) for providing a copy of the ECoS modeling framework for use in this work.

ABBREVIATIONS

AE	Assimilation Efficiency
BDAT	Bay Delta and Tributaries
BEPS	Bed Exchangeable Particles
CIMIS	California Irrigation Management Information System
DYMBAM	Dynamic Multi-Pathway Bioaccumulation Model
ECoS	Estuarine Contaminant Simulator
ETM	Estuarine Turbidity Maximum
IEP	Interagency Ecological Program
IR	Ingestion Rate
RMP	Regional Monitoring Program (in the San Francisco Bay)
NDOI	Net Delta Outflow Index
NSFB	North San Francisco Bay
POTW	Publicly Owned Treatment Works
PSP	Permanently Suspended Particles
SFEI	San Francisco Estuary Institute
TMDL	Total Maximum Daily Load
TTF	Trophic Transfer Factor
TSM	Total Suspended Material
USGS	United States Geological Survey

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EXECUTIVE SUMMARY

This document describes the development and application of a numerical model of selenium fate and transport in the North San Francisco Bay (NSFB), in support of the development of a selenium TMDL in this water body. The numerical model formulation is based on the conceptual model of selenium in NSFB that was reported earlier (Tetra Tech, 2008c). The conceptual model described the point and non-point sources of selenium to the bay and transformation and biological uptake processes in the bay. The flows and selenium loads from the Sacramento and San Joaquin Rivers are dominant in the bay, although in the dry season, some of the point sources, such as refineries, can become more important. Dissolved selenium concentrations in the NSFB are low. However, selenium present in particulate forms in the water column of the estuary bioaccumulates in filter feeders, such as bivalves, and then into predator organisms that feed on these bivalves. Selenium-associated impairment in NSFB is largely a consequence of high concentrations in these predator organisms, specifically the white sturgeon and diving ducks.

An estuary model (developed using the ECoS 3 framework) was used to simulate the selenium concentrations in the water column and bioaccumulation of selenium in the NSFB. The model built upon the previous work of Meseck and Cutter (2006). The model was applied in one-dimensional form to simulate several constituents including salinity, total suspended material (TSM), phytoplankton, dissolved and particulate selenium and selenium concentrations in bivalves and higher trophic organisms. The biogeochemistry of selenium, including transformations among different species of dissolved and particulate selenium and bioaccumulation through foodweb were simulated by the model.

Selenium species simulated by the model include selenite, selenate, and organic selenide. The particulate species simulated by the model include particulate organic selenium, particulate elemental selenium, and particulate adsorbed selenite and selenate. The uptake of dissolved selenium by phytoplankton includes uptake of three species (selenite, organic selenide and selenate). Bioaccumulation of particulate selenium to the bivalves was simulated using a dynamic bioaccumulation model (DYMBAM, Presser and Luoma, 2006), applied in a steady state mode. Bioaccumulation into bivalves considers the different efficiencies of absorption for different selenium species. Bioaccumulation to higher trophic levels of fish and diving ducks is simulated using previously derived linear regression equations by Presser and Luoma (2006), and using estimates of trophic transfer factors summarized from the literature (Presser and Luoma, personal communication, 2009). Trophic transfer factors (TTFs) are the ratio between dietary concentrations and tissue concentrations in predator organisms, and have been found to vary over a surprisingly narrow range across species and habitats. The TTFs are a relatively simple and elegant way to incorporate biological uptake from bivalves to predator species in this model.

The modeling as presented here consists of calibration and evaluation prior to its use in a predictive mode. The calibration process involves the adjustment of model parameter values to obtain the best possible fit to the measured data for selected water quality constituents that are related to selenium fate and transport. Once the parameter values have been defined through calibration, the evaluation process consists of applying the model to different time periods to compare outputs against measurements. Evaluation for time periods outside the

calibration period provides more confidence in model's ability to predict conditions that fall outside of the calibration period. The model was calibrated using salinity, TSM and phytoplankton data obtained from the USGS for 1999 and evaluated using data from 2000 through 2007. The selenium concentrations used in the model calibration were data from Cutter and Cutter (2004) and Doblin et al. (2006), which contain detailed selenium speciation information for April and November 1999. The model was evaluated using selenium data from the RMP for 2000-2005. The model performed well under different hydrological and load conditions, and was able to simulate salinity profiles and long-term patterns in TSM and chlorophyll a concentrations relatively well.

The calibrated model was also run in a hindcast mode using hydrological conditions and selenium loads for 1986 and 1998. Selenium species and loads in these periods were different from current loads, and the hindcast is another test of the credibility of the model. The simulated dissolved selenium concentrations compared well to the observed data. The model was able to simulate the mid-estuarine peaks in selenite for low flow of 1986 and 1998. This indicates that the location and magnitude of the selenium input from point sources and the transport and transformation of selenium are represented well in the model. Simulated particulate selenium concentrations also compared well with the observed values.

Although the calibration process was extensive, and generally described key constituents of interest across a range of years, seasons, and loading conditions, using a relatively small number of adjustable parameters, several features could not be fully captured by the model. This includes peaks in concentrations for constituents such as TSM and phytoplankton, represented by chlorophyll a concentrations. This is likely attributable to the limitations of the one-dimensional model in capturing the complexities of processes in the NSFB, and also to seasonal changes that were not fully parameterized during calibration. Although the model as presented here contains a great deal of the mechanistic detail associated with selenium transformations and biological uptake, it must be recognized that any one-dimensional model will have limitations in representing the full range of processes occurring in the NSFB.

Several hypothetical load reduction scenarios were presented to illustrate the relationship between sources and endpoint concentrations (dissolved, particulate, and bivalve concentrations). These load reductions are not proposed TMDL allocations but were meant to provide further insight into the estuary behavior as embodied in this model.

All scenarios consider that the Sacramento River dissolved concentrations are at a regional background level (about 0.07 $\mu\text{g/l}$), and that dissolved loads from this source are not modified. With the Sacramento River dissolved concentrations used to establish baseline conditions, changes were made to dissolved selenium loads from refineries, POTWs and other point sources, local tributaries, and the San Joaquin River. Concentrations were changed separately for the particulate load originating from the Sacramento and San Joaquin Rivers.

Particulate selenium concentrations in the flows from Sacramento River were provided as a range, reflecting the uncertainty in this input. The only available data are from Rio Vista which is tidally influenced and therefore may not represent the concentrations from the

Sacramento River. For suspended particulates the range in concentrations was 0.46 to 0.75 $\mu\text{g/g}$, and for bed exchangeable particulates, the range was 0.25 to 0.5 $\mu\text{g/g}$. Phytoplankton selenium concentrations were expressed as a Se:C ratio, and set at 15.9 $\mu\text{g/g}$ at the riverine boundary. The range of boundary conditions used for Rio Vista may be high for what is considered to be a relatively uncontaminated river, but the use of values lower than this would not be consistent with observed concentrations of selenium in particulates in the bay.

Although the dissolved and particulate loads were treated separately for the purpose of the load scenarios, once in the estuary, the forms are interrelated through the equations for uptake, mineralization, and adsorption/desorption. However, these transformations are rate limited, with literature or calibrated values of rate constants. Given the residence times in the estuary, the uptake rates provide a limit to how fast forms of selenium can change from dissolved to particulate and vice versa.

When dissolved loads, including point sources and local tributary contributions, are reduced, there are corresponding decreases in the dissolved concentrations, but minimal change in particulate species concentrations. The exception is for a tripling of the San Joaquin River dissolved load: this has a major impact on dissolved phase concentrations, and a smaller, although still significant, impact on the particulate concentrations. In comparison, a decrease of the San Joaquin River dissolved load shows limited impact on dissolved and particulate concentrations, in large part because the decrease is inundated by the contribution of the Sacramento River dissolved load. A modification of the scenario with the tripling of the San Joaquin River dissolved load (imposed by changing the concentration, but holding the flow the same as the base case) was performed by allowing delivery of Vernalis-level flows directly to the delta, with no attenuation due to aqueduct withdrawals. This resulted in a similar increase in dissolved and particulate selenium concentrations in NSFB.

A tripling and a halving of the Sacramento River particulate load only (the dissolved load was unchanged), showed a major effect on the particulate and bivalve selenium concentrations (an increase and a decrease respectively). This highlights the critical role played by this input, and the need for it to be characterized accurately. This load is different from the other loads in that it is not likely to be modified through specific actions; however, given its importance, it is poorly characterized over the period of the simulation.

The overall sensitivity of the estuary to load changes from local tributaries and point sources is greater during dry months, especially during a dry year, i.e., for a given load change factor, greater change is observed during the dry periods. This relates to the lower contribution from the Sacramento River during these periods and the longer residence times in the bay. This highlights the need for focusing on dry periods during which the impacts to the bay may be more easily observed.

The scenarios presented provide insight into the representation of the bay in the ECoS model framework, and allow evaluation of the underlying model formulation presented here. They demonstrate the somewhat different behavior of dissolved and particulate selenium over time scales and residence times that pertain to the simulation period, even though it is known that the two phases are inter-related through uptake, mineralization, and adsorption/desorption. In this regard, the model formulation is distinct from the Presser and

Luoma (2006) formulation that relates dissolved phase concentrations to particulate concentrations through equilibrium-type partitioning, with dissolved concentrations changes causing proportional changes in particulate concentrations.

The scenario calculations indicated that reducing local selenium inputs from refineries, POTWs and tributaries will result in decreases in the dissolved selenium concentrations. The decreases were not proportional to the load reductions, however, because the Sacramento River load remained constant. Importantly, changes in particulate concentrations of selenium (expressed as $\mu\text{g/g}$) are much smaller than dissolved concentration changes. For several load scenarios considered where loads were decreased, the particulate concentration changes in the bay were small. This is primarily a consequence of the existence of the baseline-level particulate concentrations that are established by the dominant Sacramento River inflows. As conceptualized in this work, and elsewhere, the uptake of particulate selenium by bivalves is a critical step in the bioaccumulation of selenium in predator organisms. The finding that during the high flow season, particulate concentrations in the bay are relatively insensitive to decreases in dissolved selenium loads is significant from the standpoint of the TMDL.

Importantly, however, the model showed that particulate load increases from the San Joaquin River could result in higher particulate concentrations (expressed as $\mu\text{g/g}$) with consequent impacts on bivalves and organisms that feed on them. When particulate loads from the San Joaquin River are lowered, particulate selenium concentrations in the Sacramento River set the lower-bound concentrations for the bay.

The combination of data and model outputs presented in this memorandum can be used to make a strong case for using this modeling approach in the development of the NSFB selenium TMDL. Although there remain areas where better fits between observations and model outputs are desirable, the limiting factor may be the use of a one-dimensional model and the absence of data to develop a more spatially and temporally resolved model. Given the present-day availability of data, the model presented here is considered suitable for conducting analyses relating selenium sources to concentrations in various biotic and abiotic compartments. The model can also be used to explore the transformations of selenium, and the fluxes between different compartments, to more fully understand the processes that result in elevated selenium concentrations found in higher-trophic level organisms in the bay.

Besides developing load allocations, the model can be used to devise monitoring strategies for different compartments and implementation strategies for attaining TMDL objectives. The model can also be used to explore system responses when conditions are very different from current conditions, with higher phytoplankton concentrations, or more extreme dry periods, for example. However, the model does not represent selenium uptake mechanistically beyond the level of the bivalves, and thus bioaccumulation into predator species is represented using previously developed regression equations (Presser and Luoma, 2006). The trophic transfer factors (TTF), which are based on kinetic uptake parameters, provide a better approach to link selenium concentrations in diets and fish tissues. The results using trophic transfer factors to link selenium concentrations in bivalves and white sturgeon tissues are also presented. Furthermore, transport to specific target organs, such as

the liver or ovaries, in species of interest, is also not considered mechanistically in this work. Controlled feeding experiments with predator species such as the white sturgeon have been reported (Linville, 2006), and depending on the nature of the target chosen for the selenium TMDL, mechanistic representation of bioaccumulation in such species may be considered in future modeling.

Overall, the modeling performed to date and the published field data incorporated in this effort, lends support to the following general conclusions of relevance to the TMDL:

- The major riverine inflows to the NSFB (Sacramento and San Joaquin) form the main loads of dissolved selenium. However, dissolved concentrations in the Sacramento River are a tenth of those in San Joaquin River ($\sim 0.07 \mu\text{g/l}$ compared to $\sim 0.7 \mu\text{g/l}$). Sacramento River flows are typically several times larger, and the dissolved load contributions from both sources to the Delta are of similar magnitude.
- The pathway of most concern from the standpoint of selenium bioaccumulation is the transfer of selenium from particulates to bivalves and the predator species that consume these bivalves.
- The selenium form of most concern in the bay is particulate selenium, which is largely supplied by the riverine loads. Selenium in the water column in the dissolved form may be converted to particulate forms, through phytoplankton uptake and adsorption, but the transformations are highly species specific: selenate interacts minimally with particles, whereas both selenite and organic selenide are more reactive. Should future efforts be focused on the derivation of a partitioning coefficient, or K_d , for selenium, the emphasis must be on deriving species-specific values. If a net K_d is estimated, representing all species of selenium, the value is highly variable depending on the season and flow conditions driven by changing selenium species in the bay.
- The bioaccumulation analysis presents a focused and possibly incomplete evaluation of the adverse effects of selenium uptake on fish and bird species that are benthic feeders. The bivalves chosen for examination in this work, *Corbula amurensis*, are very efficient at bioaccumulating selenium, more so than other bivalve species. In the bioaccumulation analysis, it is assumed that the predator species, white sturgeon and diving ducks, feed exclusively on this bivalve species. The risks to predator species in the bay from selenium uptake are very sensitive to change in the particulate concentrations because of the presence of *Corbula amurensis*, an organism that bioaccumulates Se strongly when small changes in particulate concentrations occur and pass that selenium up the benthic food web.
- From the standpoint of managing the selenium impacts to the identified biota in the bay, the most effective option is to control the particulate sources. Data from mid 1980s and late 1990s, although limited, show that dissolved and particulate concentrations do not have a simple proportional relationship in the estuary: large reductions in point source loads decreased dissolved phase concentrations, but had a small impact on particulate concentrations. The relationship between dissolved and particulate selenium concentrations in the bay is complex, and more focused data

collection and/or laboratory studies need to be performed to better characterize the transformations between different forms of selenium

- The modeling also shows that while decreases in particulate concentration (in $\mu\text{g/g}$) may be difficult to achieve, increases in concentration are possible, should there be increased loads from the San Joaquin basin by means of higher flows into the Delta. Given the range of modifications that are being proposed for the Delta waterways to improve water supplies for export, the likelihood of increased concentrations should be actively considered in the TMDL process.

The analysis presented in this work leads to the following recommendations:

- There is a need for more detailed data collection and an ongoing selenium research program in the San Francisco Bay estuary. The work presented here in some aspects relies on selenium data collected nearly a decade ago. Given the importance of selenium in the bay ecosystem, and knowledge of the pathways of bioaccumulation, a focused monitoring and research program, updated on a periodic basis, will greatly benefit selenium management in the region.
- The model simulations show that the selected particulate selenium concentrations at the system boundaries (Delta and Golden Gate Bridge) have a significant effect on the predicted particulate selenium concentrations in the water column and the bioaccumulation of selenium by clams. The modeling results are based on the use of existing data to characterize the boundary conditions. The lack of particulate selenium concentration measurements on the Sacramento River at Freeport and in the near-shore area beyond the Golden Gate Bridge is a prominent deficiency. The accurate characterization of the particulate concentrations at the boundaries of the system through field sampling efforts is essential.
- A great deal of ongoing monitoring in the bay, Delta, San Joaquin River, and aqueducts is in terms of total selenium. This study shows the limited utility of these data in characterizing bioaccumulation and ecological risk. At a minimum, such monitoring should include measurement of dissolved and particulate selenium. Monitoring must be performed using the lowest detection limits possible; much of the current routine monitoring in the Delta and aqueducts, performed with a detection limit of $0.5 \mu\text{g/l}$, shows large numbers of samples with non-detectable concentrations.
- Given the importance of the bioaccumulation of selenium and the transfer to higher organisms by *Corbula amurensis*, additional field and laboratory investigations to characterize its distribution, feeding behavior, and selenium assimilation under varying forms of selenium and particle sizes would significantly contribute the reduction in uncertainty.
- The modeling approach is able to capture the key features of selenium behavior in the system at a level that is consistent with data that can be measured. This model as currently set up can be used to explore management options in the context of the TMDL. Analysis of new speciation data with the model will be very useful.

Future model development may seek to address some of the shortcomings of the modeling presented here, such as an inability to capture the full temporal variability of ancillary parameters such as TSM and chlorophyll, the uncertainties in riverine and ocean boundary conditions and their effect on the conclusions, and the inability to reproduce the large local-scale variability in organic selenium concentrations, but such model development must be preceded by an adequate data collection program.

1. INTRODUCTION

The San Francisco Bay Regional Board is developing a selenium Total Maximum Daily Load (TMDL) for North San Francisco Bay (NSFB), due to high concentrations in some organisms. Towards that end, the Regional Board needs to conduct analyses that help explain the linkage between selenium inflows into the system and concentrations in biota of concern. In support of this effort since mid-2007, Tetra Tech has prepared a series of Technical Memorandums (TMs) focusing on individual topics of relevance to the TMDL. These TMs have included a summary of the loads of selenium to the NSFB (TM-2), a review of the selenium toxicology literature (TM-3), a conceptual model of selenium in the system (TM-4), and an overview of possible modeling approaches (TM-5) (Tetra Tech, 2008 a,b,c,d). This document (TM-6) presents the development and an application of a numerical model of selenium fate and transport in NSFB.

TMs 2-5 set the stage for the modeling presented here; this information is summarized briefly in this section, and interested readers are referred to the original documents for more detailed background information.

There has been a long history of research on selenium sources, transport, and biological uptake in San Francisco Bay, the Delta, and in the Central Valley which these series of support documents build upon (e.g., White et al., 1987, 1988, 1989; Cutter, 1989; Cutter and San Diego-McGlone, 1990; Cutter and Cutter, 2004; Presser and Luoma, 2006; Meseck and Cutter, 2006). Starting in the mid-1980's, selenium concentrations have been monitored in the bay across the salinity gradient and in different seasons reflecting variations in freshwater flows. Major sources of selenium to the Bay-Delta include:

- San Joaquin River that receives discharge from agricultural drainage from the western San Joaquin Valley
- Selenium discharged from the effluents of North Bay refineries.
- Sacramento River, which is the dominant freshwater inflow to the Bay-Delta during the wet season.
- Local tributaries (i.e., besides discharges through the Delta, largely represented by the Sacramento and San Joaquin Rivers) that discharge directly into NSFB. This may include background loads, as well as non-point loads representative of the urban and agricultural land use in their watersheds.
- Publicly owned treatment works and other NPDES dischargers that discharge directly into the bay or into tributaries near the bay.

Using flow and concentration data from each of the sources, the detailed source analysis quantified the relative magnitudes as well as the seasonal and inter-annual variability in these loads (Tetra Tech, 2008a). The average Delta load is estimated to be 3,962 kg/yr. Local tributaries draining both urban and non-urban areas are also a large source of selenium (estimated average load of 354-834 kg/yr). Refineries are now estimated to be the third largest source of selenium to the North Bay (538 kg/yr), although these loads were about three times higher prior to mid-1998 when wastewater controls were installed. Sediment resuspension/erosion and diffusion (293 kg/yr), other wastewater discharges (250 kg/yr),

and atmospheric deposition (18-164 kg/yr) are other, smaller contributors to the total selenium load. The rivers are also a major contributor of the particulate selenium load, a component that is of great significance in the uptake of selenium by bivalves and subsequently by fish.

The conceptual model presented an overview of the current understanding of selenium biogeochemistry and uptake by organisms in NSFB. Selenium behavior in three principal compartments was described, including the water column, sediments, both suspended and bedded, and biota (Tetra Tech, 2008c). This background information is summarized here.

- **Water Column:** Selenium enters NSFB in dissolved and particulate forms from the Delta, from point sources such as the refineries and municipal wastewater treatment plants, and from local tributaries. The primary sources of selenium in the suspended sediment form are the non-point sources. Phytoplankton production and sediment bed erosion are also sources. Both dissolved and particulate selenium can exist as different species that affect their cycling and bioavailability (selenate, selenite, organic selenides, and elemental selenium). Dissolved selenium can be taken up and bioconcentrated by algae and bacteria in the water column and add to the supply of particulate selenium. Selenite is the most bioavailable and bioaccumulative form of dissolved selenium. The exchange between selenate and selenite is slow, and is unlikely to occur significantly over the residence times in the bay. Conversion of selenite to organic selenide forms through microbial uptake is more rapid and is likely to be important in the bay.
- **Sediments:** Depending on the flow rate and season, deposition to and erosion from the sediment bed can also be a sink/source of particulate selenium to the water column. Sediments are more reducing than the water column, and may result in conditions that reduce selenate and selenite to elemental selenium, Se (0), a form that is insoluble and less bioaccumulative than selenite.
- **Biota:** Because of the partitioning of some forms of selenium onto particles, and the active uptake by algae, particulates in NSFB (comprising of mineral and organic particles, and live and senescing algae) are a comparatively rich source of selenium to organisms that consume them. Filter-feeding benthic organisms such as bivalves ingest and assimilate the particulate forms of selenium at different efficiencies depending on the type of particulate material. Direct absorption of dissolved selenium is minimal for organisms besides phytoplankton and bacteria. Bivalves, particularly *Corbula amurensis*, typically biomagnify selenium to concentrations higher than found in the particulate phase. When these organisms are consumed by predator species such as white sturgeon and diving ducks, the selenium is biomagnified further in the tissues of these animals. Algal and bacterial-associated selenium can also enter the food through a non-benthic pathway, i.e., through zooplankton that feed on these organisms, and through consumer organisms that feed on zooplankton. However, selenium concentrations in the non-benthic pathway foodwebs are closer to non-contaminated background concentrations.

The external source characterization, and the internal transformations of selenium set the stage for the numerical modeling presented in this document. An estuary modeling

framework ECoS 3 (v 3.39) (Gorley and Harris, 1998) was used as the basis to simulate the transport and dynamics of selenium and bioaccumulation through key elements of the food-web in the NSFB. The ultimate goal of the modeling is to relate point and non-point selenium loads to endpoint concentrations of concern, in this case concentrations in biota. ECoS 3 is a modeling framework developed by the Center of Coastal and Marine Sciences at the Plymouth Marine Laboratory, U.K. (Harris and Gorley, 1998). This modeling framework was previously applied to the NSFB to simulate the biogeochemistry of selenium by Meseck and Cutter (2006). The work presented here extends the previous work of Meseck and Cutter (2006) for the TMDL application.

Physical and geochemical processes have been studied through modeling in the San Francisco Bay over the last two decades, including hydrodynamics and salinity (Casulli and Cheng, 1992; Cheng et al., 1993; Uncles and Peterson, 1995; Gross et al., 1999; Cheng and Casulli, 2001), real-time modeling of the movement of spilled contaminants in the bay through tidal action (NOWCAST system, Cheng and Smith, 1998), suspended sediments (McDonald and Cheng, 1997), and fate and transport of PCBs (Oram et al., 2008). Besides these, two recently published models of selenium in the San Francisco Bay have also been developed (Presser and Luoma, 2006; and Meseck and Cutter, 2006).

The ECoS 3 modeling framework, and the NSFB-specific model as developed by Meseck and Cutter (2006), was selected for this modeling effort because it can be used to represent transport and biotic and abiotic selenium reactions. The model has been calibrated and evaluated using data in the NSFB. The original model has been peer reviewed and the associated computer code made available to us by the original authors. However, the model does not include bioaccumulation processes which are expected to be important for the selenium TMDL. The biological components of selenium uptake are based on the Presser and Luoma (2006) approach, which considers the uptake of selenium from the water column to bivalves, and includes uptake to higher trophic levels using trophic transfer factors between diet and predator tissue based on a review of the literature (Presser and Luoma, personal communication, 2009). TM-5 (Tetra Tech, 2008) provides more details on the model selection processes.

To model selenium in the NSFB, ancillary water quality constituents also need to be considered. Constituents simulated by the model include: salinity, total suspended material (TSM), phytoplankton, dissolved and particulate selenium, and bioaccumulation of selenium through the food-web (Figure 1-1). Salinity serves as a conservative tracer of dissolved solutes in the estuary. Dynamics of TSM reflect the transport of particulate selenium. A key process transforming selenium from the dissolved forms to the particulate forms is through phytoplankton uptake (Baines et al. 2001); therefore, simulation of dynamics of phytoplankton is also important. An important focus of the TMDL is the high selenium concentrations in water fowl and certain species of fish that feed on the benthos. Components that link particulate selenium concentrations to bivalves and predator organisms (white sturgeon and diving ducks) are included in the model. The location of NSFB and the starting point of modeling domain (the "head" of the estuary) are shown in Figure 1-2. The end of the modeling domain is at Golden Gate Bridge. For this application, the NSFB is modeled as a one dimensional, vertically well-mixed, estuary with 33 segments. The approximate locations of the 33 segments are shown in Figure 1-3.

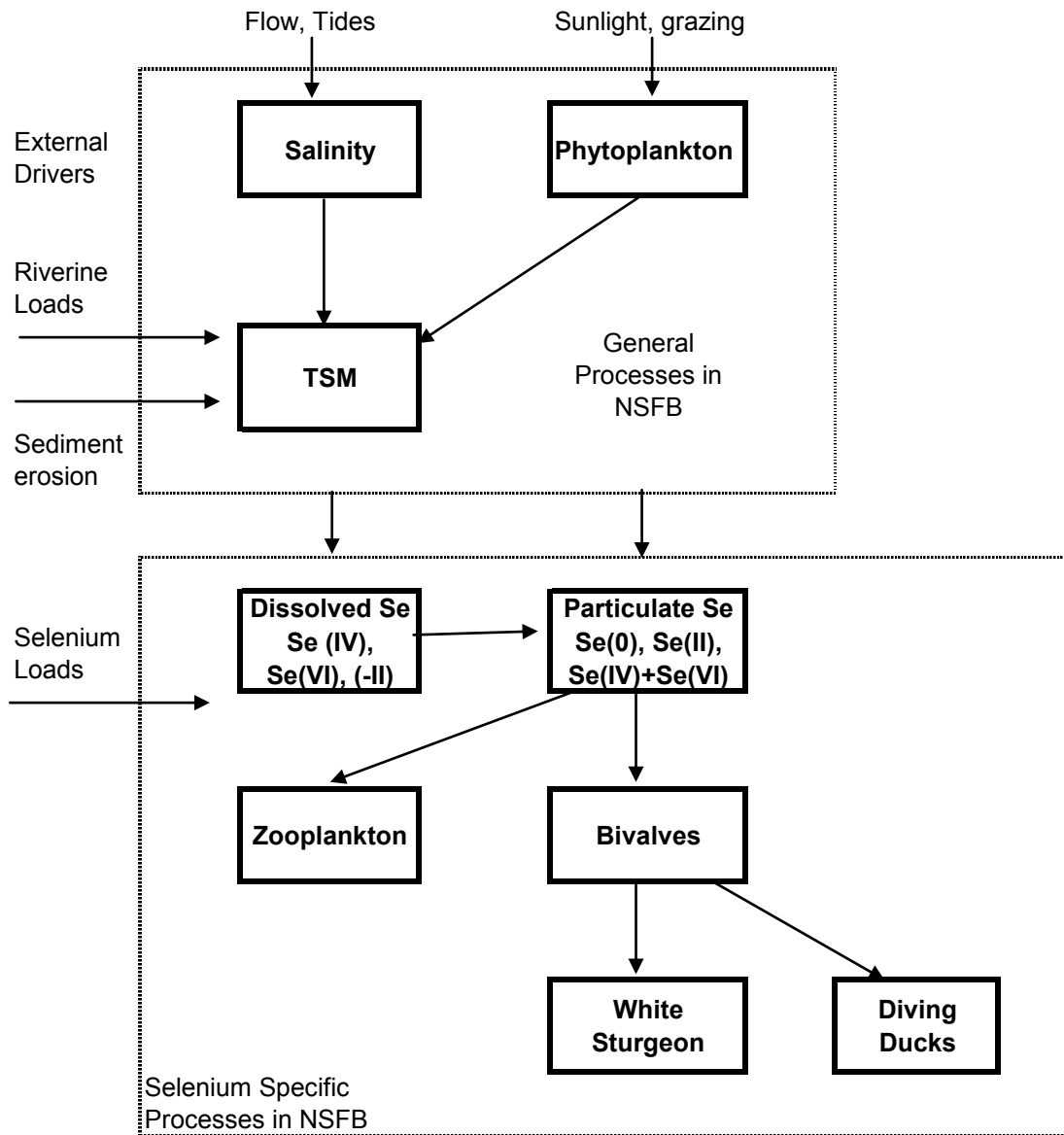


Figure 1-1 Components modeled in the ECoS3 application in NSFB.

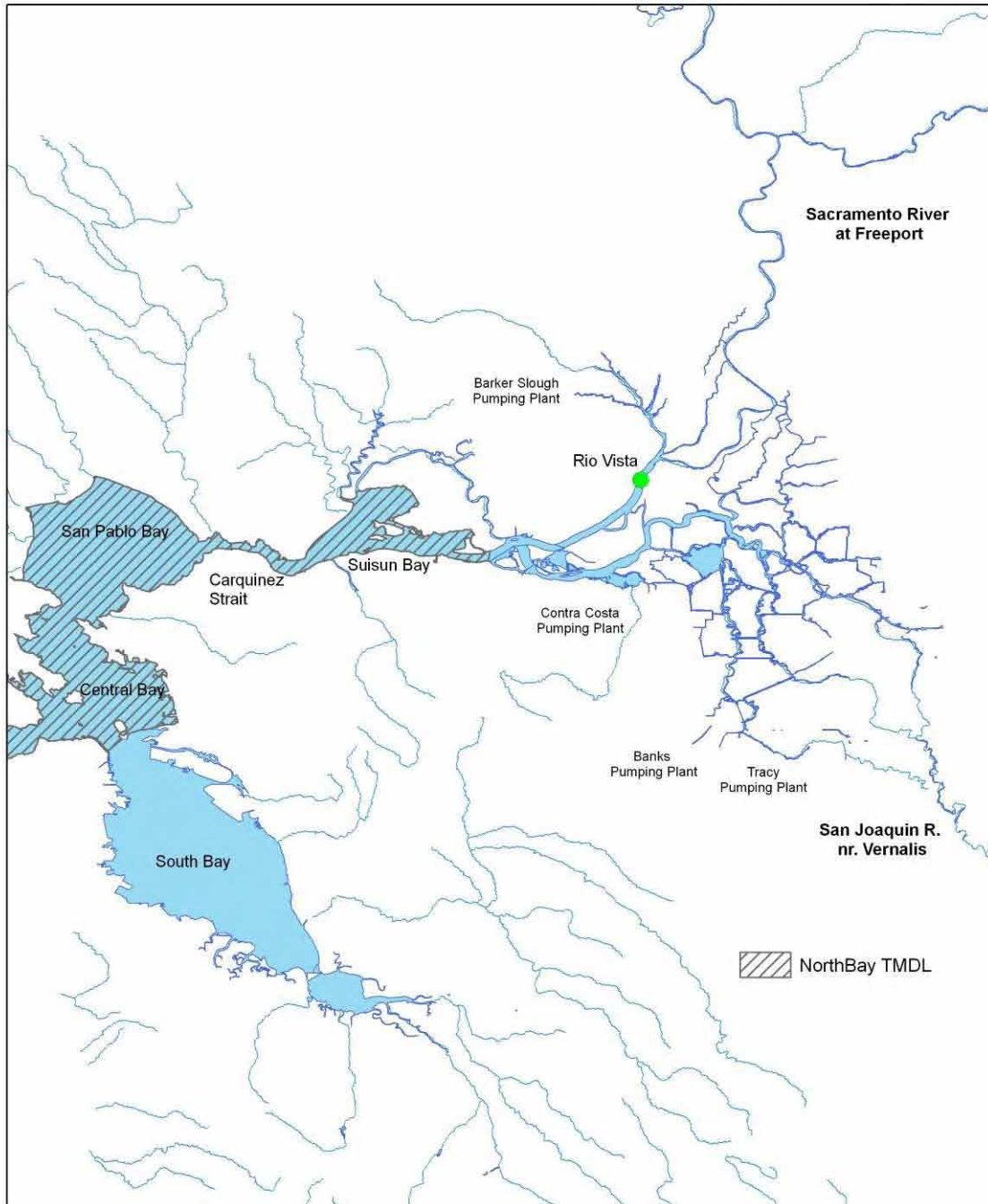


Figure 1-2 San Francisco Bay and surroundings. The model uses Rio Vista on Sacramento River as the starting point of the simulations, following Meseck and Cutter (2006). San Joaquin River inflows are added as a tributary 19 km downstream of Rio Vista. The Delta is not explicitly modeled in this application.

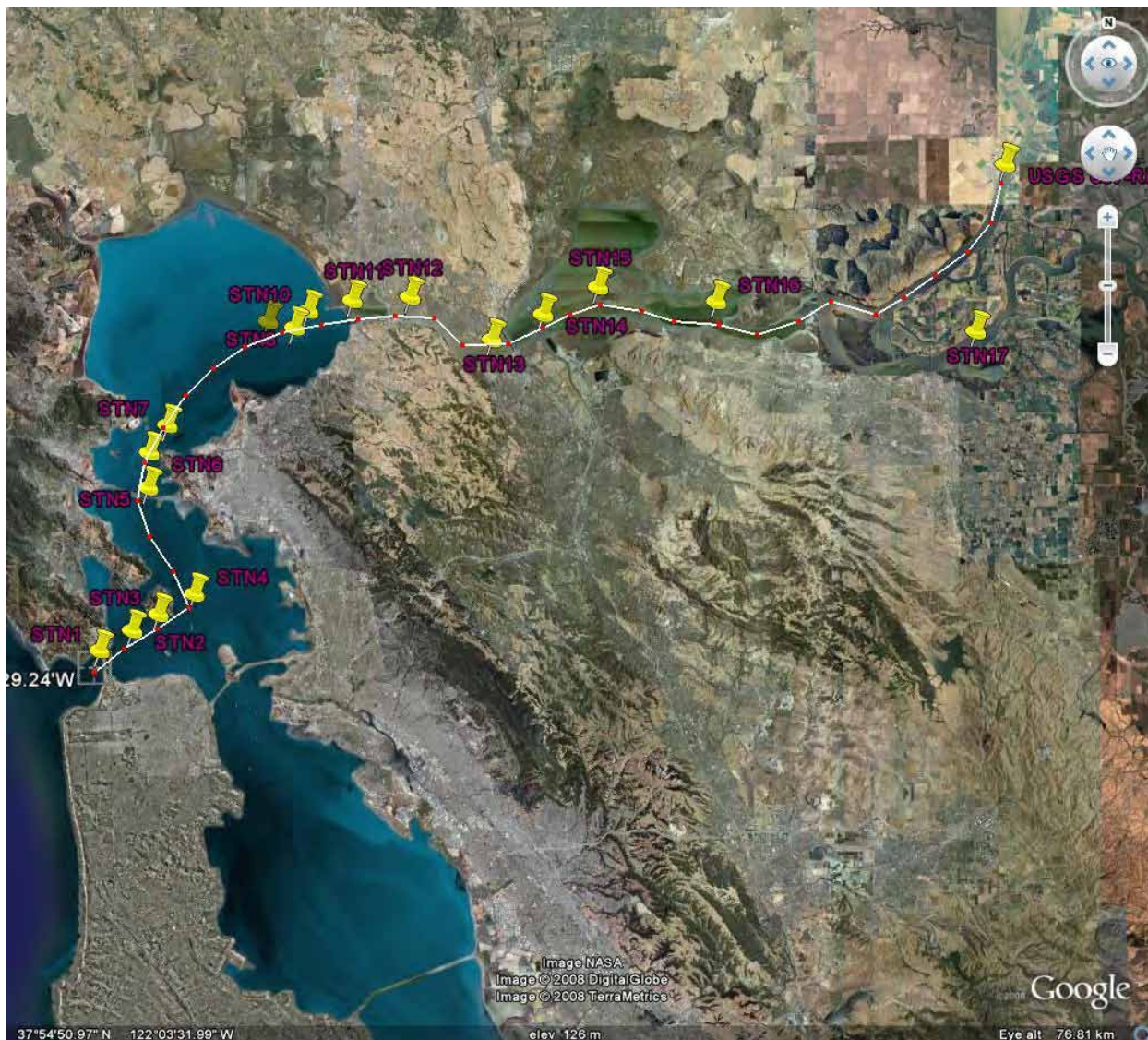


Figure 1-3 Approximate locations for 33 modeling segments in the NSFB (red dots). Yellow pins represent sampling locations in Cutter and Cutter (2004).

The purpose of the model application is to address several issues that are pertinent to the TMDL including:

1. The linkages between selenium sources and endpoints of impairment, including selenium concentrations in water column and biota.
2. Transformations between different species of selenium, and the response of particulate selenium concentrations in the bay to changes in riverine and point source loads.
3. The most effective ways of controlling selenium sources to achieve lower concentrations in particulate forms, and therefore in clams.
4. The contribution of the San Joaquin River selenium loads to the bay, and the consequences of changing this load on concentrations in biota.

5. The role of phytoplankton uptake in converting dissolved selenium to particulate selenium.

Insights developed from the modeling framework will be used to address these key issues in this document.

Modifications made to the original model of Meseck and Cutter (2006) for application in this regulatory setting can be grouped in the following general areas.

- Refinery loads: Daily selenium inputs from five refineries in the NSFB estimated based on daily flow and weekly concentrations for the period of 1999-2007 were added to model cells based on their discharge locations.
- Tributary loads: Selenium loads from local tributaries were added to the model based on their discharge locations. These loads were not identified in the prior application and may be significant in wet months.
- Publicly Owned Treatment Works (POTW) and other point source loads: Loads from POTWs and other NPDES point source dischargers in the NSFB were added to the model. Loads from these sources are smaller than other sources identified (TM-2, Tetra Tech, 2008), however they are related to the TMDL process because it is necessary to account for point source dischargers.
- Inputs of TSM and Phytoplankton from the San Joaquin River: Besides selenium inputs from the San Joaquin River, TSM loads (with TSM concentrations modeled as a function of flow) and phytoplankton loads (with observed phytoplankton concentrations) from the San Joaquin River were also added to the model.
- Sediment water interaction: Transfer between bottom sediment-associated selenium and particle associated selenium was added to the model to represent the exchange of selenium between bottom sediments and water column due to exchange of particles between the two compartments.
- Particulate selenium associated with phytoplankton: The transfer of dissolved selenium to particulate selenium through phytoplankton uptake is an important process in the bioaccumulation of selenium. Therefore particulate selenium associated with phytoplankton uptake was tracked as a separate constituent and was added to the total particulate selenium. Simulated Se:C ratio in phytoplankton was also tracked by the model and was compared to data observed for species found in the bay.
- Seawater endmember selenium concentrations: Particulate selenium concentrations at seawater end member at golden gate observed by Doblin et al. (2006) ranged between 0.8 – 1.0 $\mu\text{g/g}$, therefore a seawater endmember concentration for each species of particulate selenium was specified.
- Bioaccumulation of selenium through the food-web: A dynamic multi-pathway bioaccumulation model (DYMBAM; Presser and Luoma, 2006) was added to predict tissue selenium concentrations in bivalves; previously developed relationships between prey and predator concentrations by Presser and Luoma (2006) were used to predict bioaccumulation of selenium to the higher trophic levels.

- To better capture the salinity profile along the estuary, based on a recommendation from John Harris, a developer of the ECoS framework, salinity is modeled using a constant dispersion coefficient. This is different from the original application of the model by Meseck and Cutter (2006).

The final version of the application files for the work reported in Meseck and Cutter (2006) was not available for this work. The NSF application was reconstructed using formulations described in Meseck (2002) and the latest version of the ECoS3 manuals.¹ The reconstructed model was run under the latest available version of ECoS3 (v 3.39). Some changes in model routines have been noted in this version of ECoS3, particularly relating to TSM. The model inputs of flow from the rivers and tributaries (e.g., Napa River) as well as selenium loads were reestablished using the most recent data. The model was extended to run continuously to most current year when flow and selenium load data are available (2006-2007). The TMDL application requires the model framework to take into account selenium loads from different sources at different locations, the reconstructed model used closed riverine boundary conditions with loads instead of concentrations at the riverine boundary. Also different from the original model, each constituent, including the particulate selenium, was now modeled as a separate advecting constituent to facilitate the specification of loads at different locations (e.g., particulate selenium loads from the San Joaquin River). Taken together, the changes above entailed a reconstruction of the model code from the original Meseck and Cutter (2006) application with modifications for the TMDL purposes and updates with the newest data available, as well as a re-calibration to fit the available data.

The modeling as described here consists of calibration and evaluation prior to its use in a predictive mode. The calibration process involves the adjustment of model parameters to obtain the best possible fit to the measured data on selected water quality metrics. Once the parameters have been defined, the evaluation process consists of applying the model to different time periods to compare outputs against measurements. This evaluation process provides credibility of the model's ability to predict conditions that fall outside of the calibration period.

The model calibration and evaluation were based on salinity, TSM and phytoplankton data collected by the U.S. Geological Survey (USGS), and selenium data collected by Dr. Greg Cutter's research group at Old Dominion University (also published in several papers: Cutter, 1989; Cutter and Cutter, 2004; Doblin et al., 2006). The data used in the calibration and evaluation for salinity, TSM and phytoplankton are monthly USGS cruise data. Data from Dr. Cutter's research group are selenium speciation data under high and low flows collected in 5 sampling periods during 1997-1999. Selenium data from the Regional Monitoring Program (RMP) were also used in model evaluation. Locations of USGS monitoring stations, RMP stations, and Cutter and Cutter (2004) sampling stations are shown in Figure 1-4. A summary of data used in model calibration and evaluation is provided in Table 1-1.

¹ An early version of the model code was provided to us by Meseck after the modeling was initiated. This code was used as a reference.

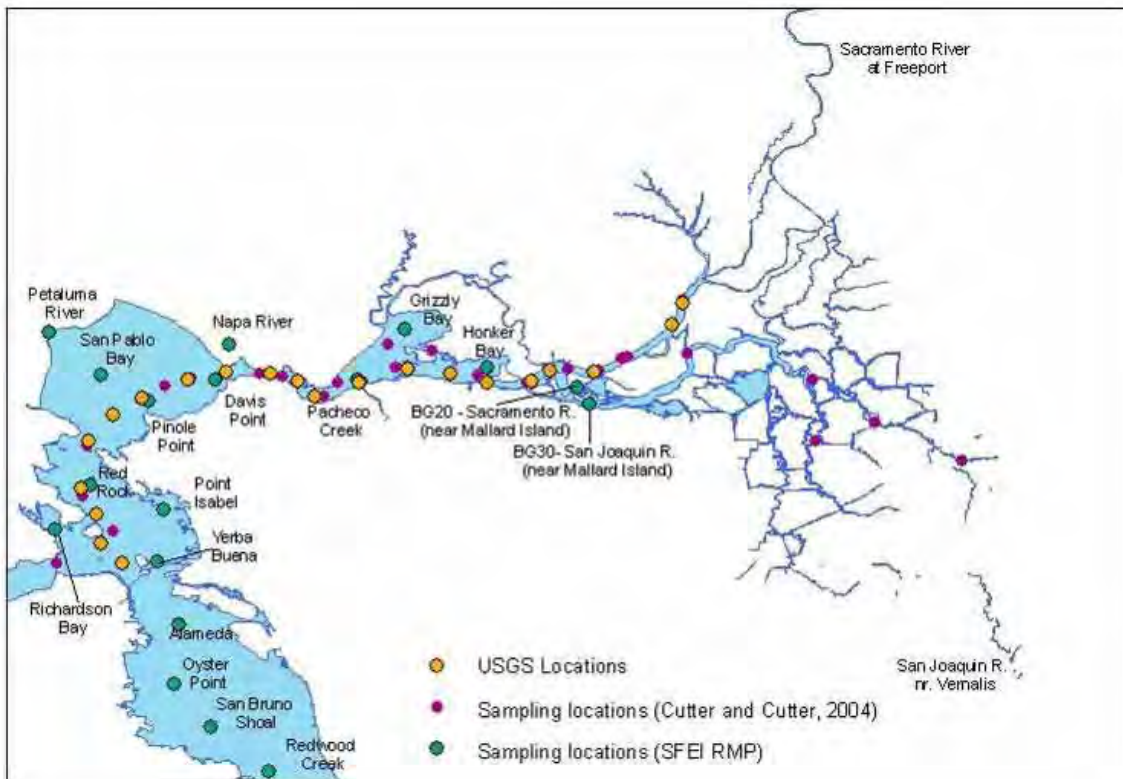


Figure 1-4 Locations of USGS gaging stations for salinity, chlorophyll a and TSM, SFEI RMP stations and sampling locations by Cutter and Cutter (2004).

Table 1-1
Data Used in Model Calibration and Evaluation

Data	Description	Source
Salinity, TSM, Phytoplankton	Monthly cruise data at about 21 locations in NSFB	USGS
Selenium Speciation Data	Dissolved and particulate selenium by species along the salinity profile for 5 sampling events during 1997-1999	Cutter and Cutter (2004); Doblin et al., (2006)
Selenium	Dissolved and particulate selenium at an interval of 2-3 sampling events per year from 1993	RMP

The remaining sections of this technical memorandum describe model formulation, calibration and evaluation, and model predictions in the NSFB. Figure 1-5 illustrates the relationship of the different analyses in this document to prior work and the final application of the model in the TMDL process. The following sections are identified in this document and in Figure 1-5.

- Section 2 Modeling Approach-Formulation and Parameterization. This section describes the basic differential equations used to represent processes of interest in selenium fate and transport. It includes representation of salinity, total suspended material (TSM), phytoplankton, dissolved and particulate selenium and selenium concentrations in biota.

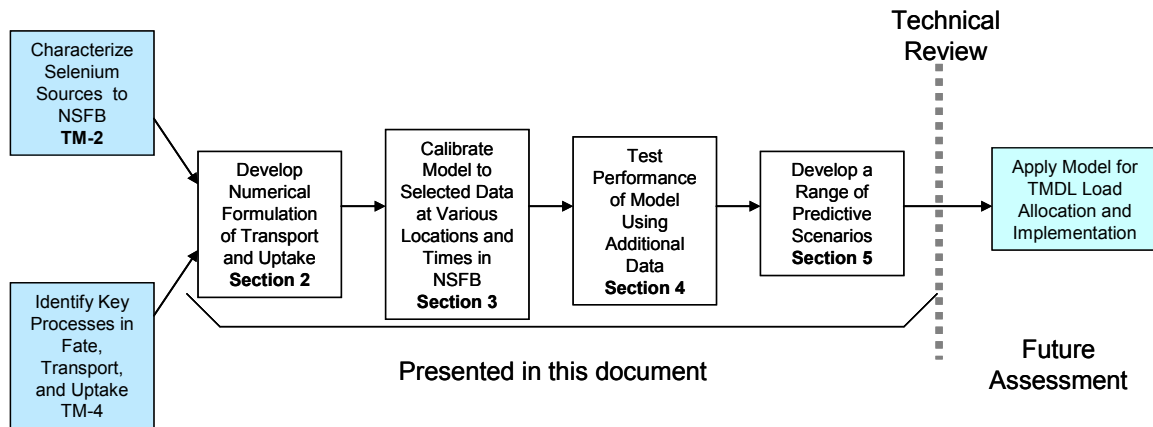


Figure 1-5 Analyses presented in this document related to prior efforts and final application of the model in the TMDL.

- Section 3. Model Calibration and Evaluation. This section describes the application of the model to a set of data from 1999 to estimate the best fit parameters for the equations representing selenium and related water chemistry (calibration). The best-fit parameters are then used to run the model for other time periods, to assess the quality of the fit under conditions different from the calibration condition (evaluation).
- Section 4. Testing Model Performance. The performance of the model is evaluated through a variety of tests, including sensitivity analysis, evaluation of fluxes between different compartments, and mass balance calculations over different time periods. The sensitivity of model outputs to perturbation of the best-fit parameters values is evaluated. Sensitivity analysis identifies parameters that have the most significant impact of model output, and can identify potential areas of weakness in the model prediction. The results of the sensitivity analysis can also help target future data collection. The other tests provide greater insight into the behavior of the model and provide simple checks on the correctness of outputs.
- Section 5. Model Predictions. The calibrated and tested model is used to compute changes in water column and biota concentrations in response to imposed changes in external loads from point and non-point sources. These model runs provide a scientific basis for considering different scenarios to attain targets in the bay.
- Section 6. Discussion. This section contains a discussion of the improved representation of selenium processes embodied in the model and potential limitations, including considerations of limited data availability, and uncertainties arising from the calibration/evaluation process.
- Section 7. Potential Use in the NSFB Selenium TMDL. This section summarizes the proposed role of the model in the TMDL process.

2. MODELING APPROACH – FORMULATION AND PARAMETERIZATION

As previously described in Harris and Gorley (1998), the ECoS3 framework contains modules that simulate transport and dynamics of different dissolved and particulate constituents in an estuary. The framework can be used to simulate dynamics of salinity, suspended sediments, phytoplankton, nutrients and metals (e.g. cadmium; Harris and Gorley, 1998). The ECoS model has been applied to the Humber Estuary of UK for salinity (Harris, 2003), suspended particles, carbon and nitrogen (Tappin et al. 2003), Tweed Estuary of UK for solute transport (Punt et al. 2003) and nutrients (Uncles et al. 2003), and Tamar Estuary for dissolved Zn and Ni (Liu et al. 1998). The ECoS3 software package is a modeling framework that can be applied as 1-D or 2-D form (Harris and Gorley, 2003). The modular structure of the framework allows cut and paste model development. The NSF B application by Meseck and Cutter (2006) is used to simulate different species of selenium.

The dynamics of constituents are generally modeled as a result of advection, dispersion and in-situ transformation:

$$\frac{\partial s}{\partial t} = U \frac{\partial s}{\partial X} - \frac{\partial}{\partial X} (Kx \frac{\partial s}{\partial X}) - \Gamma \quad (1)$$

Where U = velocity, Kx = dispersion coefficient, Γ = in-situ transformation, s = solute concentration and X = length along the estuary. For each time step, the model calculates changes due to *in situ* transformations and then calculates changes due to transport. The initial concentrations and changes in concentrations are used to predict concentrations for the next time step.

Meseck and Cutter (2006) added equations to simulate transport and transformations of different species of selenium in the NSF B. For the Meseck and Cutter application, the NSF B was modeled as a 1-D well-mixed estuary with 33 segments. The model domain starts from freshwater end member at the Sacramento River at Rio Vista ($X = 0$ m; head) and extends to the mouth at Golden Gate (total length = 101,000 m). The head of the estuary is modeled as a closed boundary with seawater as open boundary. The Meseck and Cutter (2006) spatial representation was used in this work.

Selected data elements, relating to ancillary parameters such as TSM and chlorophyll a, are included in Section 2, where relevant to the model formulation process or to the specification of boundary conditions. Model calibration data are introduced in Section 3.

2.1. SALINITY

The dynamics of salinity along the estuary are a result of mixing of freshwater and seawater, driven by freshwater inflow, wind and tides. During the high flow season, freshwater advection dominates and lower salinity through the estuary is observed. During low flow, salinity in the estuary increases as a result of decreases in freshwater input. Accurate simulation of salinity along the longitudinal transect of the estuary indicates that advection and dispersion of dissolved solutes are simulated correctly. In ECoS3, salinity can be modeled as a result of advection and dispersion (Harris and Gorley, 1998; Meseck, 2002):

$$\frac{\partial S}{\partial t} = -U \frac{\partial S}{\partial x} + K_w \frac{\partial^2 S}{\partial x^2} \quad (2)$$

where U is the water velocity, S is salinity, and K_w is the dispersion coefficient along the axis (X) of the estuary. Freshwater input at the head of the estuary is assumed to have a salinity of 0 and seawater is assumed to have a salinity of 32 psu. The dispersion coefficient is modeled as a single constant which is a calibrated parameter. Water velocity is calculated as flow divided by cross section areas, derived from the Uncles and Peterson (1996) model.

2.2. TRANSPORT OF SEDIMENT

The potential sources of sediments to the bay include the Delta input, local tributaries, *in situ* resuspension and erosion, and *in situ* production due to phytoplankton growth. In ECoS3, two different types of suspended sediment materials are modeled: the permanently suspended particles (PSP) and bed exchangeable particles (BEPS). For the NSFB application, another component of the TSM, phytoplankton, is added to the model. TSM is modeled as the total of PSP, BEPS and phytoplankton biomass:

$$TSM = PSP + BEPS + B \quad (3)$$

where B is phytoplankton biomass (described in the following section 2.3).

The PSP is suspended material that does not sink and does not interact with the bottom sediments, and is modeled in a manner analogous to a dissolved solute (Harris and Gorley, 1998; Meseck, 2002). The dynamics of the PSP is modeled as:

$$\frac{\partial PSP}{\partial t} = -U \frac{\partial PSP}{\partial x} + K_w \frac{\partial PSP}{\partial x^2} + PSP_{river} \quad (4)$$

where PSP_{river} is the riverine input of permanently suspended material (mg/l/d). In ECoS, riverine input of PSP is specified as riverine PSP concentrations, multiplied by flow. Previous studies have found that Sacramento River is the dominant source of suspended sediments to the Bay and discharges seven times more suspended sediments to the Bay the other tributaries including the San Joaquin River (Meseck, 2002). In this application, sediment inputs from the San Joaquin River were also added to the model.

BEPS originates from sediment resuspension. A small portion of the BEPS also originates in the riverine input. Dynamics of BEPS in the estuary reflects sediment-water interaction. BEPS is modeled as a result of sediment resuspension and deposition, as well as advection and dispersion. In the NSFB, an estuarine turbidity maximum (ETM) can form due to tidal asymmetry (Schoellhamer, 2001).

In ECoS3, the tidally averaged sediment transport velocity for BEPS is modeled as:

$$U_{beps} = d * (U - e * R * S) \quad (5)$$

where U is the seaward water velocity (m/d), R is the tidal range at mouth (m), and S is salinity. Both d and e are calibration parameters. Parameter d scales the axial velocities in

relation to water velocity and the parameter e scales the up-estuary component relative to the seaward transport, and determines the position of the estuary turbidity maximum. Increasing e moves the turbidity maximum up-estuary. The value of d is usually less than 1 since particle velocity is generally less than water velocity (Harris and Gorley, 1998). Dispersion of BEPS is proportional to mixing due to both freshwater movement and tides.

$$K_{beps} = \varepsilon * U + \psi * R * S \quad (6)$$

where ε and ψ are calibration coefficients. Similar formulations were used in simulating transport of suspended particles in the Humber Estuary by Tappin et al. (2003), and a reasonable fit between simulated and observed PSP was found.

Sediment deposition rate is in proportion to BEPS and is modeled as deposition velocity divided by water depth.

$$MD = V_s/H \quad (7)$$

where V_s is sediment deposition velocity (m/d) and H is water depth (m). Deposition is most significant where the BEPS maximum is found. Sediment deposition velocity was 86.4 m/day based on work by McDonald and Cheng (1997). It was assumed that the total flux of sediments from the estuary bed to the water column is balanced by deposition. Two previous studies from USGS found that NSFB including the San Pablo Bay and Suisun Bay on net is eroding (USGS 2001a, b). The average net erosion rate was estimated to be small, at a value of 0.0063 kg/m²/d. To reflect this effect, sediment resuspension rate is specified as deposition rate plus this net erosion rate.

Little is known regarding the variation in bottom sediment mass across the estuary. Based on a previous literature review, the active sediment depth of the NSFB is assumed to be 15 cm (Leatherbarrow et al. 2005). Similar to Davis (2003), using a sediment density of 2.7 g/m³ and a solids concentration in sediment of 0.5, the active sediment bed mass is 130.5 kg/m².

It was found that spring-neap tidal variations can be significant. Tides are mixed diurnal and semidiurnal and the tidal range varies from about 0.6 m during the weakest neap tides to 1.8 m during the strongest spring tides (Schoellhamer, 2001).

Tidal variation can be simulated using a six component tidal model as in Meseck (2002):

$$TIDE = M_2 + S_2 + K_2 + O_1 + M_4 + M_6 \quad (8)$$

where each component of the tide is defined as:

$$TC(i) = TA(i) * COS((TP(i) - TF(i)*T) * \pi/180) \quad (9)$$

where $TC(i)$ is the tidal constituent (e.g. M_2 , S_2 , K_2), TA is tidal amplitude (m), TP is tidal phase (degrees), TF is the tidal frequency (degrees/day or degrees/hr), $\pi/180$ converts the angles of tidal frequency and phase to radians. Main components of tides in Golden Gate are M_2 (0.58m), K_1 (0.37m) and O_1 (0.23m) (Uncles and Peterson, 1996).

2.3. PHYTOPLANKTON

The dynamics of phytoplankton play an important role in regulating selenium transformations. Dissolved selenium can be taken up by phytoplankton to form particulate organic selenium, which is bioavailable to higher trophic level organisms (Luoma et al. 1992). Phytoplankton dynamics in the NSFB are a function of different sources and sinks. Species and concentrations of phytoplankton vary with season and river flow, with lower phytoplankton concentrations coincident with higher river flow (Cloern et al. 1983). Phytoplankton in the estuary is subjected to loss due to respiration, benthic grazing and zooplankton grazing. Benthic grazing can be a controlling factor in phytoplankton biomass (Lucas et al. 2008). Due to the invasion of Asian clam *Corbula amurensis* in NSFB beginning in 1985, dramatic decreases in chlorophyll a concentrations were observed (Alpine and Cloern, 1992). Chlorophyll a concentrations have shown some slight increases in the San Pablo and Central Bays in recent years (Cloern et al. 2006, Figure 2-1).

The NSFB receives high nutrient loadings, and the growth of phytoplankton is considered to be light limited (Cole and Cloern, 1984). Vertical mixing in the NSFB is relatively rapid. Data from USGS monthly cruise sampling suggests relatively uniform chlorophyll a concentrations along the depth profile (Figure 2-2). Therefore, phytoplankton concentrations are assumed to be completely mixed vertically for this effort.

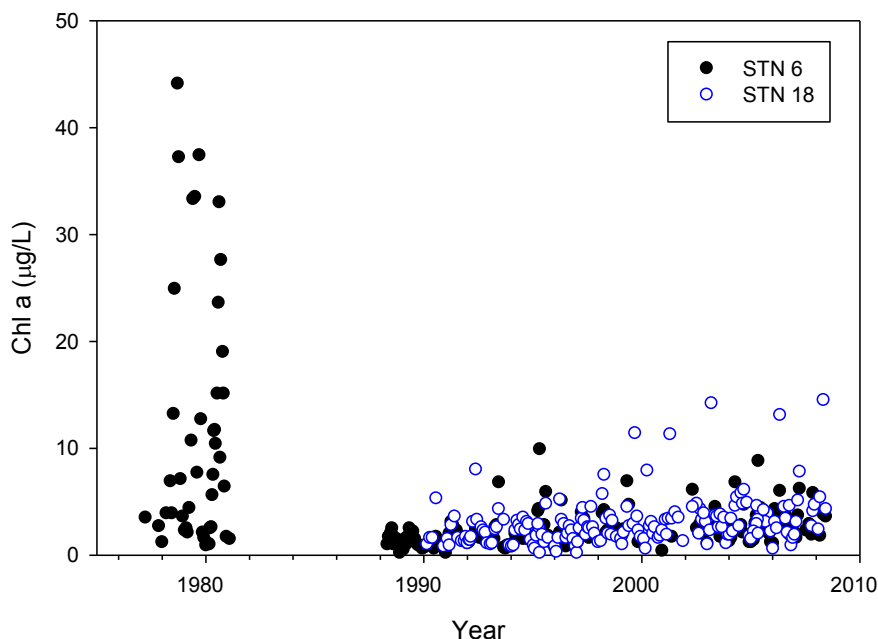


Figure 2-1 Long-term chlorophyll a concentrations in Suisun Bay (STN 6) and Central Bay (STN 18).

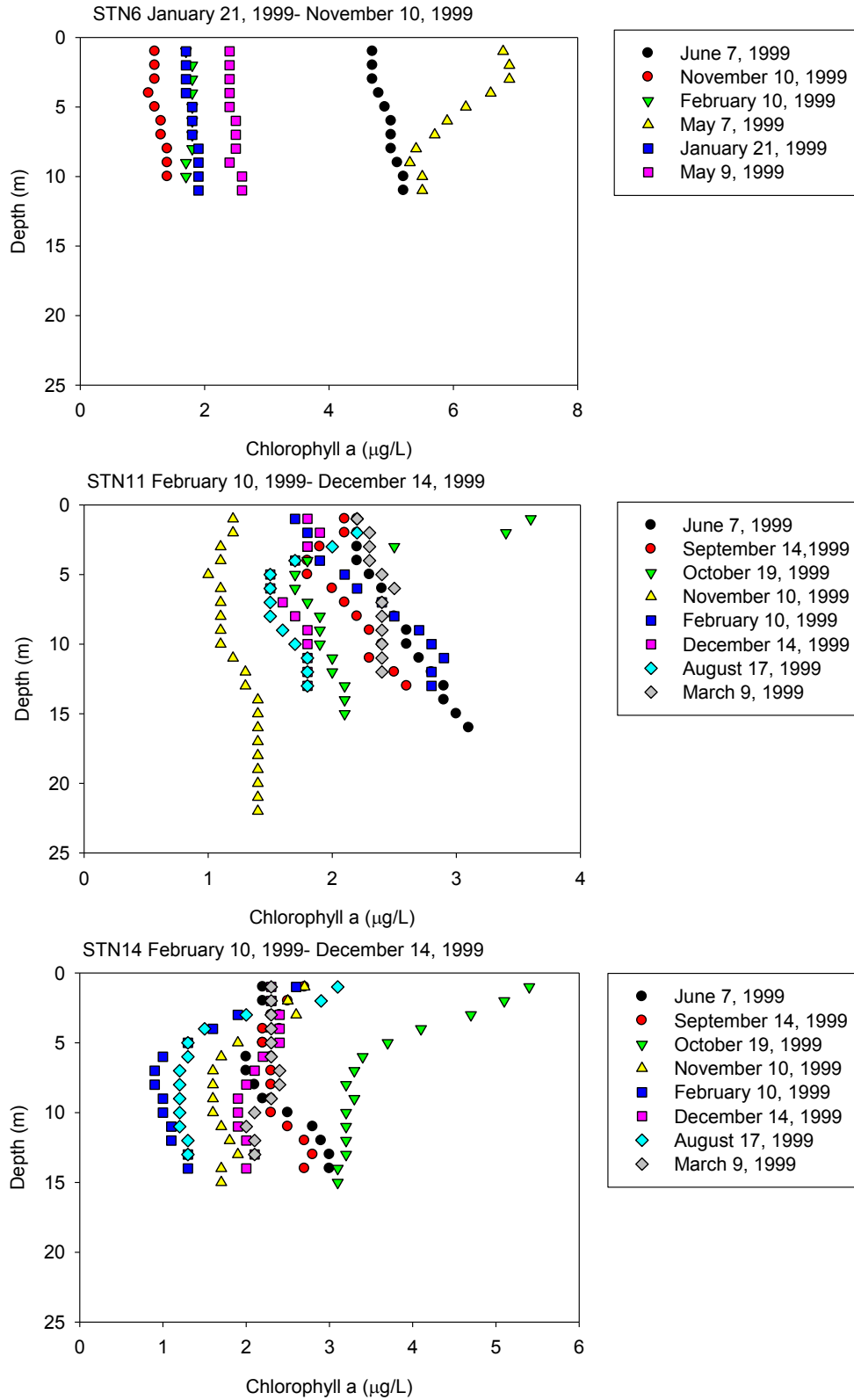


Figure 2-2 Depth profiles of chlorophyll a concentrations at stations STN 6, STN 11 and STN 14 for year 1999.

For the application in the NSFB, phytoplankton dynamics are affected by transport, growth, grazing by zooplankton and benthic organisms, settling, respiration and riverine input (Meseck, 2002).

$$\frac{\partial B}{\partial t} = -U \frac{\partial B}{\partial x} + Kx \frac{\partial^2 B}{\partial x^2} + \mu_n B - GB - P_b B - \frac{\partial}{\partial z}(wsB) - RB + B_{river} \quad (10)$$

Where B is the phytoplankton biomass (mg/l), μ_n is net biomass-specific growth rate (d^{-1}), G is the grazing due to zooplankton (d^{-1}), P_b is the benthic grazing rate (d^{-1}), ws is the sinking velocity of phytoplankton (d^{-1}), R is the respiration rate (d^{-1}) and B_{river} is the riverine input of phytoplankton (mg/l/day). Sinking of phytoplankton was found to be between 0.5 – 0.9 m/d and is set to be at 0.5 m/d (Cloern 1991; Kosseff et al. 1993; Lucas et al. 1998). Phytoplankton mortality is due to respiration losses and grazing effects. Mortality due to respiration can be up to 10% of the maximum rate of photosynthesis and is held constant at this value in the model (P_m ; mg C/mg Chl/d, Cole and Cloern, 1984). The benthic grazing rate was mostly due to benthic clams such as *Corbula amurensis* after the introduction in 1985. Based on studies by Werner and Hollibaugh (1993), *C. amurensis* has the potential to graze phytoplankton at rates greater than the specific growth rate of phytoplankton and was specified at a constant rate of 0.04 d^{-1} . Benthic grazing rates were found to vary across season and location (Thompson et al. 2008). Grazing by zooplankton is simulated as a function of zooplankton abundance and ingestion rates of phytoplankton per animal based on weight (Cloern et al, 1985; Appendix 2). Zooplankton abundance varies with space and time and ranges between 13 – 330 organisms/liter (Figure 2-3). The weight of zooplankton ranges from 7 to 63 μg C/organism (Hutchinson, 1981).

The growth rate of phytoplankton is a function of light (Platt and Jassby, 1976). The biomass-specific rate of photosynthesis is modeled as:

$$P = P_m \tanh(\alpha I) \quad (11)$$

where P_m is the maximum rate of photosynthesis at optimal light intensity (mg C/mg Chl/d), α is the initial slope of the light-saturation curve divided by P_m (m^2 d/Einst), and I is the photosynthetically active radiation (PAR, Einst/ m^2 /d). In the northern reach, P_m varies from 24 to 219 mg C/mg Chl/d (Cloern and Alpine, 1991). The values of α varies from 0.002 to 0.009 Einst. m^2 /d (Lucas et al., 1998). Net biomass specific growth rate μ_n is simulated as P divided by carbon chlorophyll a ratio. Irradiance of light at depth z is modeled as:

$$I(z) = I_\lambda e^{-kz} \quad (12)$$

where k is the attenuation coefficient of light within the water column (m^{-1}) and z is water depth (m; Miller and Zepp, 1979). In a well-mixed water column the irradiation can be simulated as:

$$I = I_\lambda \left(\frac{1 - e^{-kz}}{kz} \right) \quad (13)$$

The attenuation coefficient k is defined as:

$$k = k_w + k_d + k_p + k_s * TSM \quad (14)$$

where k_w is the scattering of light due to water (m^{-1}), k_d is due to dissolved matter (m^{-1}), k_p is due to phytoplankton (m^{-1}), and k_s is due to non-living suspended material (L/g/m). The sum of k_w and k_d is set to $0.1 m^{-1}$ based on calculations by Miller and Zepp (1979).

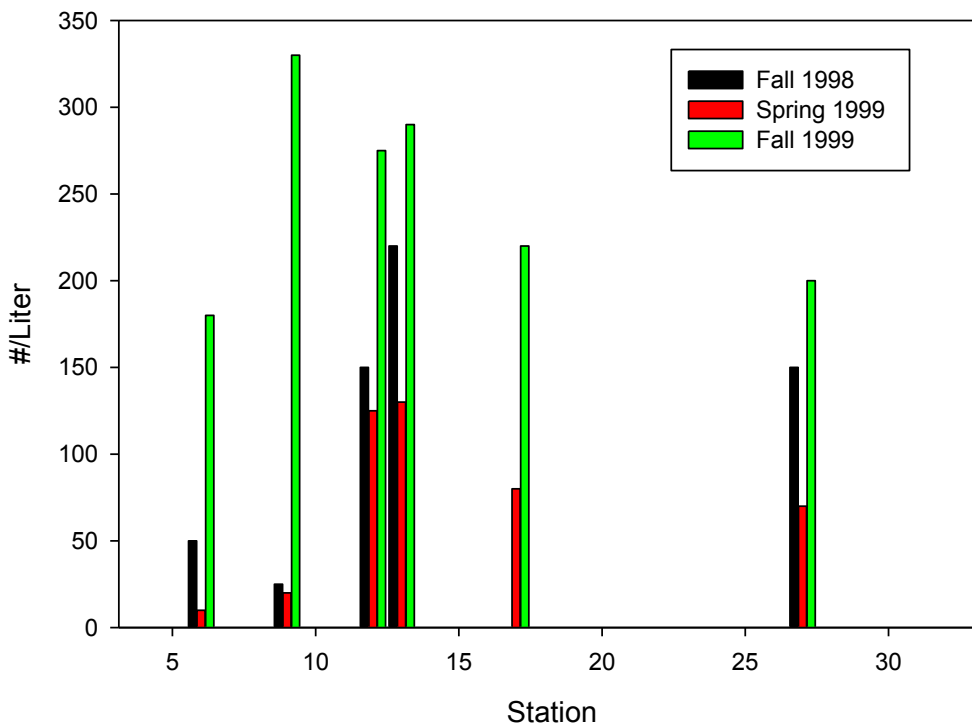


Figure 2-3 Zooplankton abundance sampled by Pukerson et al. (2003) for stations across the Bay.

2.4. DISSOLVED SELENIUM

Dissolved selenium can enter the NSFB from the Delta, local tributaries, refineries, municipal and industrial wastewater discharges, and sediment diffusion. The sources and potential transformations are shown schematically in Figure 2-4. Speciation of selenium from these sources is generally dominated by selenate (Se(VI)), followed by organic selenide (Se(-II)) and selenite (Se(IV)). While in the water column, different species of selenium can undergo biological and chemical transformations. Transformations of dissolved selenite include oxidation to selenate, uptake by phytoplankton and adsorption and desorption from minerals. Transformations of dissolved organic selenide include oxidation to selenite and uptake by phytoplankton. Dissolved organic selenide is also generated through mineralization of particulate organic selenide. For selenate, the transformation includes uptake by phytoplankton and microbes. Oxidation of selenite to selenate was found to be a slow process which can take hundreds of years, while oxidation of organic selenide to

selenite occurs over a timeframe of weeks (Cutter, 1992). Phytoplankton uptake of dissolved selenium, particularly for selenite, was found to occur relatively rapidly (Riedel et al. 1996; Baines et al. 2004). Uptake of organic selenide was found to occur at approximately the same rate with selenite, followed by selenate. Data on microbial population and uptake of selenium are not available in the bay.

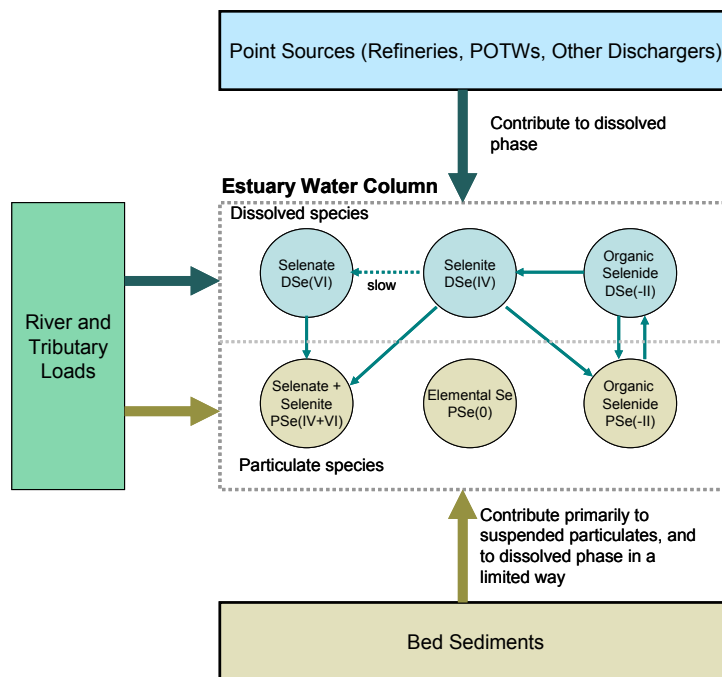


Figure 2-4 Schematic of selenium sources and transformations in the water column of the estuary. Point sources are primarily in the dissolved form, and sediment erosion contributes mostly to suspended particulates. River and tributary loads can include both dissolved and particulate selenium.

Dissolved selenium dynamics are modeled as a result of point and non-point source inputs, advection and dispersion, as well as *in situ* transformation. Transformations between species such as oxidation and uptake by phytoplankton are simulated as first-order kinetic reactions. Transformation processes of different species of selenium modeled are:

$$\frac{\partial DSe(VI)}{\partial t} = k_3[DSe(IV)] - k_5[DSe(VI)] + b[PSe(IV)] - a[DSe(IV)] \quad (15)$$

$$\frac{\partial DSe(IV)}{\partial t} = k_2[DSe(-II)] - k_3[DSe(IV)] - k_4[DSe(IV)] \quad (16)$$

$$\frac{\partial DSe(-II)}{\partial t} = k_1[PSe(-II)] - k_2[DSe(-II)] - k_6[DSe(-II)] \quad (17)$$

where the rate constant k_1 is the mineralization rate of particulate organic selenide to form dissolved organic selenide. Mineralization of organic selenide was found in a previous study to be a pseudo first-order (Cutter and Bruland, 1984). Rate constants k_2 and k_3 are for

oxidation of organic selenide to selenite and selenite to selenate respectively. Constants k_4 - k_6 are used to model phytoplankton uptake of selenite, selenate and organic selenide, respectively. D and P refer to dissolved and particulate phases in the water column, and a' and b relate to adsorption/desorption processes. The uptake and transformation processes are shown schematically in Figure 2-5. For some reactions, a wide range of rate constants was reported in literature, and therefore calibration was needed as described in Section 3. Table 2-1 lists values for the rate constants reported in the literature. Note that rates of uptake from Riedel et al. (1996) and Baines et al. (2004) are absolute rates measured under very different ambient selenite concentrations (10 $\mu\text{g/L}$ and 0.02 $\mu\text{g/L}$). The uptake rates are shown in Table 2-1 as both absolute rates used in the original references and as uptake rate constants (1/g chl a/hr, in parentheses). The uptake rate constants are not dependent on ambient selenium concentrations. The uptake rates are shown for easy comparison to the original references and for comparison across the two literature sources.

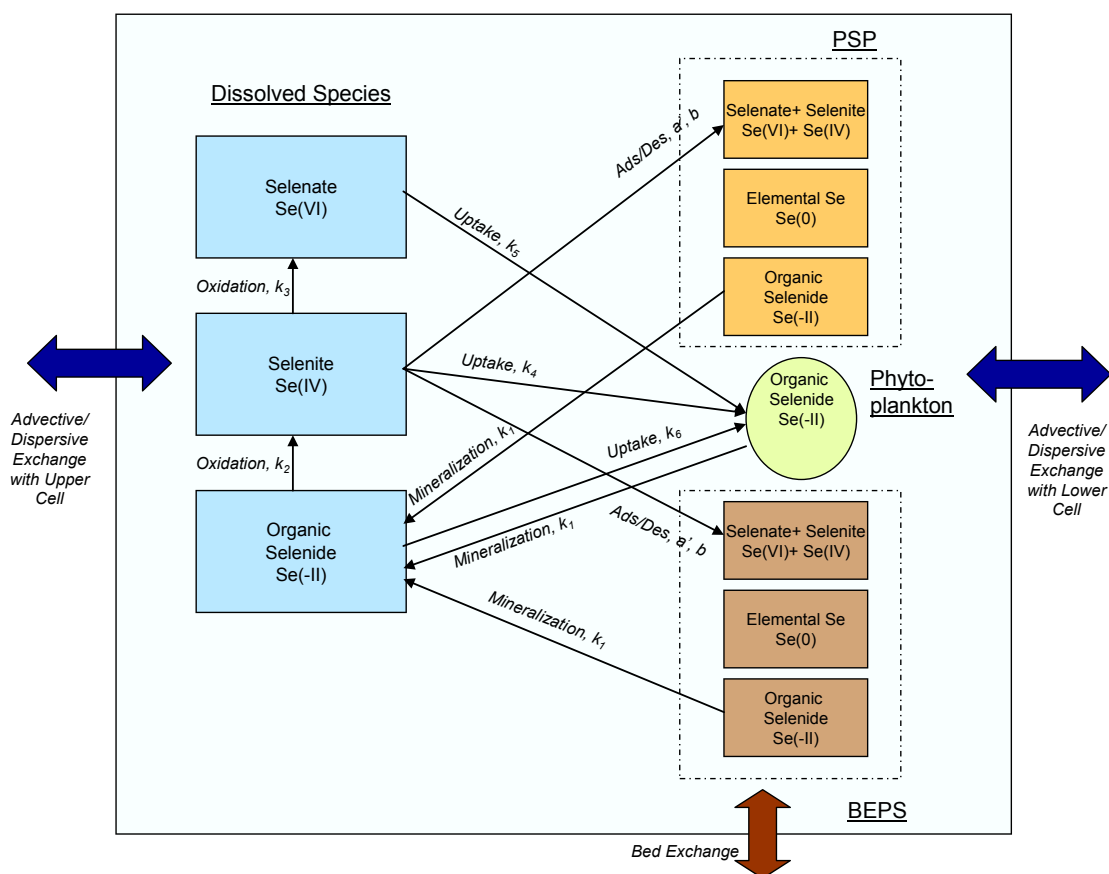


Figure 2-5 Representation of selenium exchanges between different compartments in each cell of the model. Transformations are shown for each species in the dissolved and particulate phases (PSP, permanently suspended particulates; phytoplankton; and BEPS, bed exchangeable particles).

Table 2-1
Literature values for first order rate constants

Constant	Process	Description	Value	Unit	Reference
k ₁	P Se(-II) → D Se(-II)	Mineralization of particulate organic selenide	1.3×10 ⁻⁵ - 5×10 ⁻²	d ⁻¹	Regeneration experiments (Cutter, 1992)
k ₂	D Se(-II) → D Se (IV)	Oxidation of dissolved organic selenide	1.0×10 ⁻³ - 81.0	d ⁻¹	Surface and deep Pacific water (Suzuki et al. 1979, cited in Cutter, 1992)
k ₃	D Se(IV) → D Se (VI)	Oxidation of dissolved selenite	2.4×10 ⁻⁶	d ⁻¹	Deep Pacific, Cutter and Bruland (1984)
k ₄	D Se(IV) → P Se (-II)	Uptake of dissolved selenite by phytoplankton	2.02-2.41 (15.8- 18.8) 0.07-0.21* (225.8- 777.8)*	μmol Se (g chl) ⁻¹ hr ⁻¹ (l/g chl a/hr) pmol Se (ug chl) ⁻¹ hr ⁻¹ (l/g chl a/hr)	Riedel et al. (1996) Baines et al. (2004)
k ₅	D Se(VI) → P Se (-II)	Uptake of dissolved selenate by phytoplankton	0.43-0.58	μmol (g chl) ⁻¹ hr ⁻¹	Riedel et al. (1996)
k ₆	D Se(-II) → P Se (-II)	Uptake of dissolved organic selenide by phytoplankton	0.5 k ₄	μmol (g chl) ⁻¹ hr ⁻¹	Baines et al. (2001)
a'	D Se(IV) → PSe (IV)	Mineral adsorption of selenite	0.1-0.8	l/g/d	Zhang and Sparks (1990)
b	PSe(IV) → D Se(IV)	Desorption of adsorbed selenite	Kd/a'	d ⁻¹	Zhang and Sparks (1990)

* Values taken are measured rates for two sites (Channel and Chlorophyll maximum) during evening and morning, excluding abiotic uptake in the dark.

Sediment diffusion of selenium was found to be a very small flux based on estimates from Meseck (2002). In the study, fluxes from sediments were estimated as a function of diffusion coefficient and measured concentration gradient in pore water, as well as irrigation by bivalves. In Meseck (2002), the following equation was used in estimating the sediment diffusion:

$$J = - \Phi * D_s * \delta Se / \delta z + \sum Z_i \lambda_i (C_w - C_i) \quad (18)$$

Where J is the sediment diffusion flux (nmol/cm²/yr), Φ is the porosity, D_s is the effective diffusion coefficient (5.83 × 10⁻⁶ cm² s⁻¹), $\delta Se / \delta z$ is the observed concentration gradient of pore water selenium, z_i is the depth of sediment zone i (2 cm), λ_i is the irrigation coefficient (s⁻¹; 20 × 10⁻⁷ s⁻¹), C_w is the overlying water concentration, and C_i is the average pore water concentration at depth i . Total selenium fluxes to water column were estimated to be

relatively small. A recent update of the study suggests the flux of selenate was into the sediment at a rate of 0.01 nmol/cm²/yr (S. Meseck, personal communication).

2.5. PARTICULATE SELENIUM

Particulate selenium may be present in the following forms: particulate elemental selenium, adsorbed selenite and selenate and particulate organic selenide. Particulate selenium in the estuary can originate from riverine input, sediment resuspension, and in-situ transformation. A large amount of sediments and living/non living particulate organic material enters the bay through the rivers. Sediment loads from the Delta were estimated previously by McKee et al. (2006) to range from 0.26 to 2.6 million tons/yr. Different species of particulate selenium are assumed to be associated with PSP and BEPS. Phytoplankton selenium is assumed to be present only as organic selenide. Riverine inputs of particulate selenium are specified as selenium content by different species on riverine loads of particulates (PSP, BEPS, and phytoplankton). Although phytoplankton can be measured as part of the TSM, here phytoplankton is modeled separately and as is the phytoplankton-associated particulate organic selenium. Particulate organic selenium associated with PSP is assumed to be selenium associated with organic carbon other than living phytoplankton (e.g., detritus of phytoplankton, plant material, bacteria).

Selenium contents on riverine PSP are calibrated parameters that are bounded by values in Doblin et al. (2006). Selenium contents on riverine phytoplankton uptake are specified at 15.9 µg/g Se:C (Baines et al. 2004). The value was measured as the uptake ratio of selenite and carbon by plankton from incubation experiments using water collected from a site in the Delta. Particulate selenium associated with BEPS is subjected to exchange with particulate selenium in bed sediments at the same rates of sediment resuspension and deposition. Seawater end member concentrations of particulate selenium are specified as constants (as selenium content on seawater concentrations of PSP) for an open boundary. The transfer from dissolved selenium to particulate selenium includes mineral adsorption (mostly for selenite) and phytoplankton uptake of dissolved selenium for all three dissolved selenium species.

Particulate elemental selenium can be formed through dissimilatory reduction of selenite and selenate in anoxic environments. For NSFb, the water column is oxic, therefore particulate elemental selenium mostly originates from Delta input or in the bed sediment. Particulate elemental selenium is modeled as a result of riverine input, sediment resuspension, and transport processes, and is not produced in the water column of the bay.

$$\frac{\partial PSe_o}{\partial t} = -U \frac{\partial PSe_o}{\partial x} + K_x \frac{\partial^2 PSe_o}{\partial x^2} + Se_{o,SED} * \frac{\partial BEPS_{riv}}{\partial t} + Se_{o,river} * \frac{\partial PSP_{riv}}{\partial t} \quad (19)$$

For particulate adsorbed selenite and selenate, besides inputs from riverine and exchange with the sediments, particulate selenite and selenate are subject to adsorption/desorption.

$$\frac{\partial PSe_{IV+VI}}{\partial t} = -U \frac{\partial PSe_{IV+VI}}{\partial x} + K_x \frac{\partial^2 PSe_{IV+VI}}{\partial x^2} + Se_{IV+VI,SED} * \frac{\partial BEPS_{riv}}{\partial t} + Se_{IV+VI,river} * \frac{\partial PSP_{riv}}{\partial t} \quad (20)$$

$$+ a' DSe(IV) - b * PSe_{IV+VI}$$

where a' is the intrinsic adsorption rate constant (L/g/d) and b is the desorption rate constant (d^{-1}).

The adsorption of selenate is considered to be negligible in the Bay water given the high pH. Most studies on selenite and selenate adsorption and desorption are related to soils (Zhang and Sparks, 1990). Selenate adsorption to mineral surfaces was non site-specific and involves the outer sphere complex. Adsorption of selenite is site specific and involves ligand exchange. Therefore the adsorption of selenate is weaker than that of selenite. Both reactions are dependent on pH, with increasing pH resulting in decrease in selenite adsorption (Neal et al., 1987).. It was found that at pH 6, adsorption of selenate is non-detectable. Due to the high pH in the estuary (>6), adsorption of selenate is minimal and only adsorption of selenite is considered (Meseck, 2002). Selenite adsorption was found to occur rapidly in freshwater (i.e., within 60 seconds; Zhang and Sparks, 1990), while desorption is found to occur at a much slower rate.

Zhang and Sparks (1990) found that a' ranges from 0.1 to 0.8 L/g/d. Desorption rate b can be derived as:

$$b = \frac{a'}{K_d} \quad (21)$$

where K_d is partition coefficient for selenite (L/g). For freshwater, K_d ranges between 0.5 to 2.5 L/g (Zhang and Moore, 1996). K_d for selenite based on data from November 11, 1999 averages at 13.3 L/g. For some trace elements such as cadmium, due to competition for adsorption sites, the adsorption decreases as salinity increases:

$$K_d = K_0 * (S + 1)^{-b} \quad (22)$$

where K_0 is the partition coefficient in fresh water where salinity is zero and b is coefficient that dictates the rate of decreases with salinity (Bale 1987). For selenite, derived K_d values do not show a significant relationship with salinity, therefore b is set to 0 for selenite adsorption.

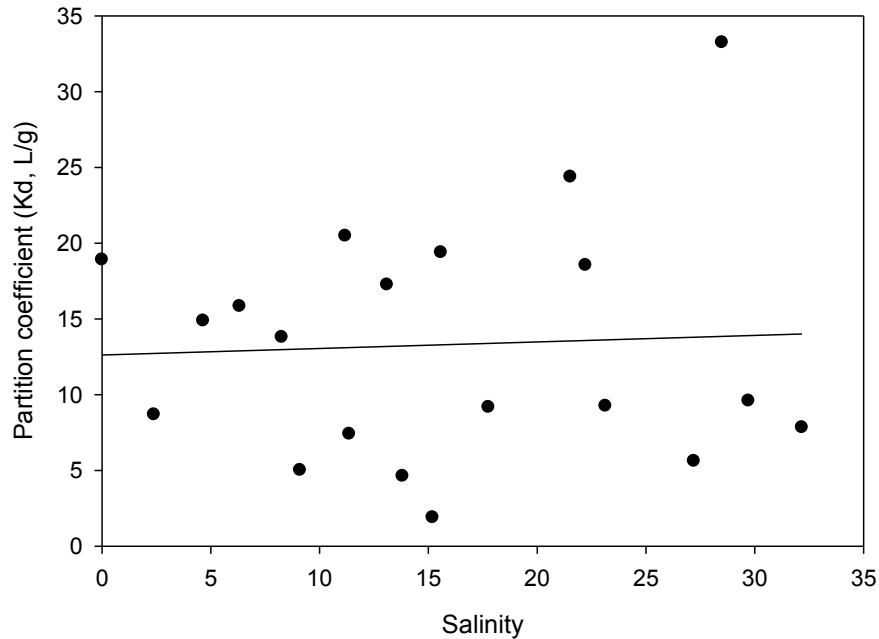


Figure 2-6 Partition coefficient (Kd) of particulate adsorbed selenite and selenate over selenite as a function of salinity in the NSFB (Source: Cutter and Cutter, 2004).

For particulate organic selenium, transformations also include uptake by phytoplankton and mineralization to dissolved organic selenide. Dissolved organic selenide is then oxidized to selenite.

$$\frac{\partial PSe(-II)}{\partial t} = -U \frac{\partial PSe(-II)}{\partial x} + K_x \frac{\partial^2 PSe(-II)}{\partial x^2} + Se_{-II,SED} * \frac{\partial BEPS_{river}}{\partial t} + Se_{-II,river} * \frac{\partial PSP_{river}}{\partial t} + P_{uptake} - k_1[PSe(-II)] \quad (23)$$

Uptake by phytoplankton is calculated as:

$$P_{uptake} = k_4 * [DSe(IV)] + k_5 * [DSe(VI)] + k_6 * [DSe(-II)] \quad (24)$$

Rate constants of phytoplankton uptake and mineralization of particulate organic selenide were discussed previously in Section 2.4. With the kinetic uptake rates by phytoplankton and adsorption/desorption from mineral particulates, the partitioning between dissolved and particulate selenium is modeled as a dynamic process instead of a being defined by a constant partition coefficient.

Selenium in sediments is modeled as a combination of initial concentration modified by resuspension and deposition through sediment-water interaction, as well as some riverine input. The initial concentrations of selenium in sediments by different species were data from Meseck (2002) along the length of the estuary. Sediment concentrations at the surface (<15 cm) were dominated by elemental selenium (60%), followed by organic selenide (20-25%) and particulate selenite and selenate (15-20%). Due to the balanced resuspension and

deposition rates of sediment, the modification of selenium concentrations in bottom sediments is small.

In this document, particulate concentrations are expressed as $\mu\text{g/l}$ or as $\mu\text{g/g}$ depending on the context. The former approach is needed for mass balance type calculations, in that it is a representation of the amount of selenium in a given volume, the latter approach is useful for computing uptake by filter feeders such as bivalves, but without TSM information, does not have any significance in a mass balance calculation.

2.6. SELENIUM UPTAKE BY BACTERIA AND PHYTOPLANKTON

Dissolved selenium in the water column can be directly taken up by phytoplankton and bacteria. Selenium exists in reduced organic forms within algal or bacterial cells or is exuded as dissolved organic selenium. Organic selenium in algal cells is highly bioavailable to organisms that consume them, such as zooplankton and bivalves (Luoma et al., 1992; Schlegel et al., 2000). Therefore, uptake of selenium by bacterial and planktonic organisms is important in evaluating selenium bioaccumulation.

Algal selenium uptake by phytoplankton varies widely across species. Cellular selenium concentrations for nine species of marine algae vary by an order of 10^5 (Baines and Fisher, 2001). Cellular selenium concentrations of various phytoplankton species are shown in Table 2-2. Se:C ratios measured by Doblin et al. (2006) were in atomic units and were converted to $\mu\text{g/g}$. For NSFB, algal species vary with season and location and over the long term there has been a shift in species (Lehman et al., 2000). In the winter, phytoplankton biomass in the upper estuary is comprised of freshwater diatoms and while in spring blooms marine centric diatoms dominate (Cloern et al., 1985). Over the long-term, there has been a decrease in diatoms and increases in chlorophyte, cyanophyte and flagellates. Recent sampling in 2006-2007 by Lidstrom and Carpenter (2008) also indicated that there have been decreases in diatoms and increases in small cells such as flagellates and picoplankton. Although large variations exist even within the same group (e.g. diatoms show large variations in Se:C ratio across species), selenium concentrations in phytoplankton generally following the order of: golden brown algae > dinoflagellates > diatoms > green algae. The four groups of phytoplankton compared here are used as general groupings. It was also found that phytoplankton during wet and normal years are more dominated by diatoms, green, bluegreen and chrysophytes, while during dry and critically dry years, cryptophytes, green flagellates and miscellaneous flagellates dominate.

During low flow conditions higher salinities could be encountered in the northern parts of the estuary in which freshwater phytoplankton cannot survive. However, under those conditions, marine phytoplankton species are likely to replace freshwater organisms. In this case, freshwater phytoplankton may be mineralized (if not grazed) to dissolved organic selenide, and may be taken up by marine phytoplankton.

The phytoplankton uptake of selenium is treated as one single component and not as two groups of species (marine and freshwater). As long as there is phytoplankton present in the estuary, there is assumed uptake of selenium by phytoplankton.

Table 2-2
Cellular selenium concentrations (ng/μm³) for marine algae exposed to 0.15 nM (11.84 ng/l) selenite (from Baines and Fisher, 2001; after Abu Saba and Ogle, 2005).

Taxonomic Class	Algal Species	Cellular Se Concentration (ng/μm ³)*	Cellular Carbon Concentration (pg C/μm ³)*	Se:C Ratio (μg/g)*	Particulate Se (μg/g dwt exposed to 90nM Selenite)**
Bacillariophyceae (diatoms)	<i>Skeletonema costatum</i>	4.95 x 10 ⁻¹³	0.14	0.004	3.08
Chlorophyceae (green algae)	<i>Chlorella autotrophica</i>	4.73 x 10 ⁻¹¹	0.22	0.215	3.63
Chlorophyceae (green algae)	<i>Nannochloris atomus</i>	5.46 x 10 ⁻¹¹	0.22	0.248	3.31
Chlorophyceae (green algae)	<i>Dunaliella tertiolecta</i>	1.21 x 10 ⁻¹⁰	0.17	0.712	3.87
Bacillariophyceae (diatoms)	<i>Chaetoceros gracilis</i>	3.31 x 10 ⁻¹⁰	0.14	2.364	3.00
Bacillariophyceae (diatoms)	<i>Thalassiosira pseudonana</i>	1.09 x 10 ⁻⁹	0.16	6.813	5.21
Dinophyceae (dinoflagellates)	<i>Prorocentrum minimum</i>	3.08 x 10 ⁻⁹	0.13	23.692	13.49
Cryptophyceae (golden brown algae)	<i>Cryptomonas sp.</i>	4.90 x 10 ⁻⁹	0.16	30.625	ND
Prymnesiophyceae	<i>Emiliania huxleyi</i>	3.37 x 10 ⁻⁸	0.22	153.182	ND

* Data from Baines and Fisher (2001)

** Data from Doblin et al. 2006 converted from atomic ratios to μg/g based on atomic weights of Se (78.9) and C (12).

ND = No data

Selenium uptake exhibits cellular regulation behavior, with cellular selenium concentrations showing less variation corresponding to changes in ambient selenium concentrations in the water column (Baines and Fisher, 2001; Table 2-2). For the diatom *Thalassiosira pseudonana*, the half saturation was found to be at a low concentration of 0.2 nmol/L (0.016 μg/L; Baines and Fisher, 2001). Michaelis-Menton kinetics types of equations can be used in simulating the saturation uptake. However, due to large variations in cellular concentrations among species and the uncertainties in algal species composition in NSFB, the selenium uptake by phytoplankton is modeled using first-order uptake rates without differentiating the algal species, similar to the approach used by Meseck (2002). Model-predicted selenium concentrations in phytoplankton (in terms of Se:C ratio) were compared to observed values in the seston of the Delta (Baines et al., 2004). The Se:C ratio in phytoplankton is calculated as selenium concentrations associated with phytoplankton (μg/L) divided by phytoplankton biomass (in units of carbon, g C/L).

Limited phytoplankton species data for recent years are available from Environmental Monitoring Program (EMP) of Interagency Ecological Program (IEP; http://www.baydelta.water.ca.gov/emp/Stations/station_index.php?station=D41). The data

suggest large variations in species through time and increased flagellates in recent years as shown in a station (D41) in San Pablo Bay, one of the five locations in the Bay sampled for phytoplankton species (Figure 2-7). For station D41, phytoplankton species were dominated by flagellates in recent years of 1999-2003 and by golden brown algae and green algae for 2004-2006 (Figure 2-6). Selenium concentrations in phytoplankton when dominated by green algae are likely to be lower than when dominated by golden brown algae. Cellular selenium concentrations in flagellates however have not been measured in previous studies. Three of the phytoplankton species, *Skeletonema costatum* (diatom), *Rhodomonas salina* (cryptophyte) and *Prorocentrum minimum* (dinoflagellate), are important species found in the San Francisco Bay (Lehman 1996).

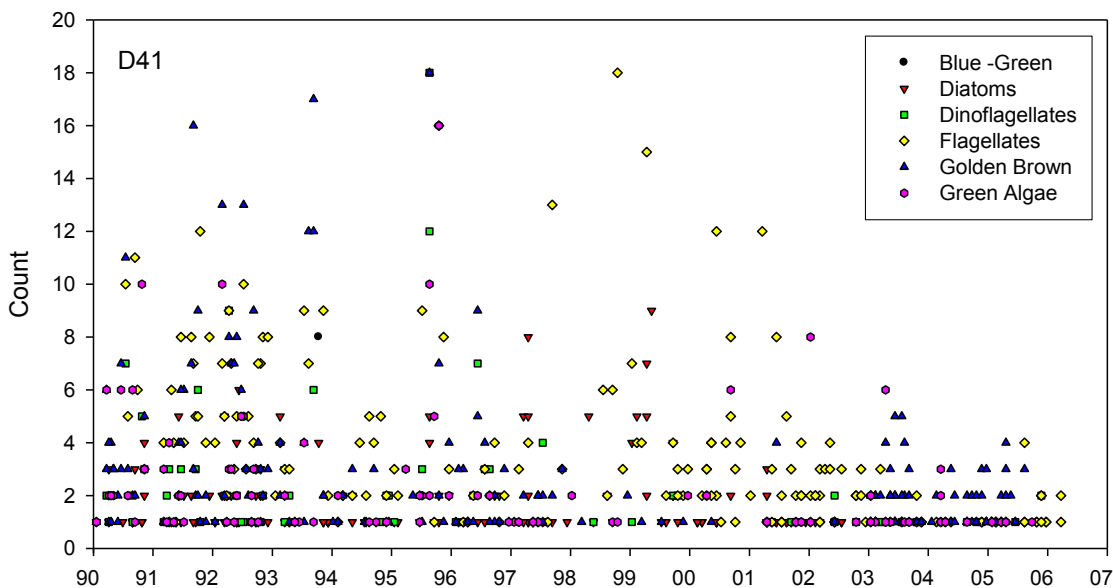


Figure 2-7 Phytoplankton species data from a station in San Pablo Bay (D41) as a function of time (Data Source: IEP).

2.7. SELENIUM UPTAKE BY ZOOPLANKTON AND BIVALVES

Accumulation of selenium to the higher trophic levels through consumption of zooplankton or bivalves has significant implications in the TMDL. Fish that feed on benthic invertebrates were found to accumulate higher concentrations of selenium in their livers (Stewart et al. 2004). Accumulation of selenium in zooplankton or bivalves is mostly through the food-borne route, through the ingestion of particulate selenium (Luoma et al., 1992). Direct uptake of dissolved selenium was found to be minimal. Different origins or different species of particulate selenium differ in the assimilative efficiency to bivalves. Generally, organic-associated particulate selenium such as detritus of phytoplankton or particulate elemental selenium produced through biological reductions are more bioavailable to bivalves than mineral associated particulates (Schlekat et al., 2000).

The modeling of accumulation of selenium in zooplankton or bivalves follows a previously developed metal bioaccumulation model in the bay. The model is the dynamic multi-pathway bioaccumulation model (DYMBAM; Luoma et al., 1992; Stewart et al., 2004;

Presser and Luoma, 2006). The model predicts metal concentrations in bivalve tissues using concentrations in food, food ingestion rate, metal assimilation efficiency, and elimination rate. Parameters for different metals and different species of organisms have been quantified in various studies (reviewed by Luoma and Rainbow, 2005). The filter-feeding *C. amurensis* was found to have higher assimilation efficiency and lower elimination rate, and thus accumulates selenium to higher concentrations than resident bivalves (Lee et al., 2006; Linville et al. 2002).

To predict tissue concentrations in the bivalve *C. amurensis*, the DYMBAM model formulation was added to ECoS. In DYMBAM, accumulation of particulate selenium through lower trophic level organisms is based on dietary and waterborne uptake. The dynamic form of the model is as follows:

$$\frac{dC_{mss}}{dt} = k_u \times C_w + AE \times IR \times C_f - k_e \times C_{mss} \quad (25)$$

where C_{mss} is selenium concentration in tissue ($\mu\text{g/g}$), k_u is the dissolved metal uptake rate constant (L/g/d), C_w is the dissolved metal concentration ($\mu\text{g/L}$), AE is the assimilation efficiency (%), IR is the ingestion rate (g/g/d), C_f is the metal concentration in food (e.g. phytoplankton, suspended particulate matter, sediment) ($\mu\text{g/g}$), and k_e is the efflux rate (d^{-1}). Uptake through the waterborne pathway was found to be negligible (Luoma et al., 1992). Parameter values of DYMBAM model for uptake of selenium by *C. amurensis* are derived from Stewart et al. (2004; Table 2-3).

Table 2-3
Parameters for DYMBAM model for *Corbula amurensis*

<i>K_u</i> (L/g/d)	<i>IR</i> (g/g/d)	<i>AE</i> (%)	<i>K_e</i> (d⁻¹)	Growth Rate (/d)	Tissue Se Concentration (mg/kg)	Reference
0.003	0.25	45-80	0.025		2.1-12.0	Stewart et al. (2004)
0.009	0.1-1.0	36(sediment) 54(algae)	0.023	0.005	3.9-20.0	Lee et al. (2006)

In the model, the steady state formulation of equation (21) is used. The bioaccumulation of bivalves through time can be modeled through integrating the above equation through time with an initial concentration. The results are similar to steady state formulation except for the period of ramping up of the model and therefore the steady state equation is used. AE for different species of particulate selenium for *Corbula amurensis* derived from literature are listed in Table 2-4. Assimilation efficiencies measured by Schlekot et al. (2002) are in a relatively narrow range for different species of algae and are generally high. AE for elemental selenium are generally low, with biogenic particulate elemental selenium showing higher AE . Assimilation efficiency measured by Lee et al. (2006) for algae was at a lower value of 54%, which may be due to low spiked selenium concentrations used in algae (two orders of magnitude lower than that observed in SFB waters) and mixture of sediment with algae in the food. Different ingestion rates have also been estimated for *Corbula amurensis*. The ingestion rates estimated by Lee et al. (2006) show a wide range of 0.1 to 1.0 g/g/day (Table 2-3). The ranges in assimilation efficiency and ingestion rates were used to forecast the range of selenium concentrations in bivalves (Table 2-5 and Box 1). In the model

predictions of different scenarios, an AE of 0.2 or 20% was used for particulate elemental selenium. An AE of 45% was used for particulate adsorbed selenite + selenate, and an AE of 80% was used for particulate organic selenium. Ingestion rates used in model predictions range between 0.25 to 0.85 g/g/day (Table 2-5) and an ingestion rate of 0.45 g/g/day was used in model scenario predictions. Assimilation efficiency for particulate organic selenium has generally been determined using living phytoplankton although tests with sediments have also been performed.

Table 2-4
Literature values of assimilation efficiencies (AE) for *Corbula amurensis*

Species	AE	Origin	Reference
Se(0) ²	2%	AA – reduction of SeO ₃ ²⁻ to Se(0) through ascorbic acid (AA)	Schlekat et al. (2000)
Se(0)	7 ± 1%	SES – reduction of SeO ₃ ²⁻ to Se(0) through pure bacteria culture (SES)	Schlekat et al. (2000)
Se(0)	28 ± 15%	SED – reduction of SeO ₃ ²⁻ to Se(0) through sediment microbial consortium (SED), biogenic origin	Schlekat et al. (2000)
Selenoanions	11%	Reoxidized sediment slurries	Schlekat et al. (2000)
Organoselenium	53%	Ph. Tricornutum	Schlekat et al. (2000)
<i>Cryptomonas sp.</i>	88.9%	Algae cells	Schlekat et al. (2002)
<i>Gymnodinium sanguinem</i>	82.6%	Algae cells	Schlekat et al. (2002)
<i>Phaeodactylum tricornutum</i>	80%	Algae cells	Schlekat et al. (2002)
<i>Synechococcus sp.</i>	78.3%	Algae cells	Schlekat et al. (2002)
<i>Thalassiosira pseudonana</i>	87.3%	Algae cells	Schlekat et al. (2002)
Sediment	36%	Fresh water stream, San Jose, CA	Lee et al. (2006)
Algae (mixed with sediment)	54%	Diatan, <i>Phaeodactylum tricornutum</i>	Lee et al. (2006)

Table 2-5
Parameters for DYMBAM Model Used in Model Simulations

Parameter Set	IR	AE (particulate elemental selenium, PSe0)	AE (particulate adsorbed selenite and selenate, PSeivvi)	AE (particulate organic selenium, POrgSe)
1	0.45	0.2	0.45	0.8
2	0.25	0.2	0.45	0.8
3	0.45	0.2	0.45	0.54
4	0.85	0.2	0.45	0.80

² This form of elemental selenium does not occur in nature and was synthesized in the laboratory.

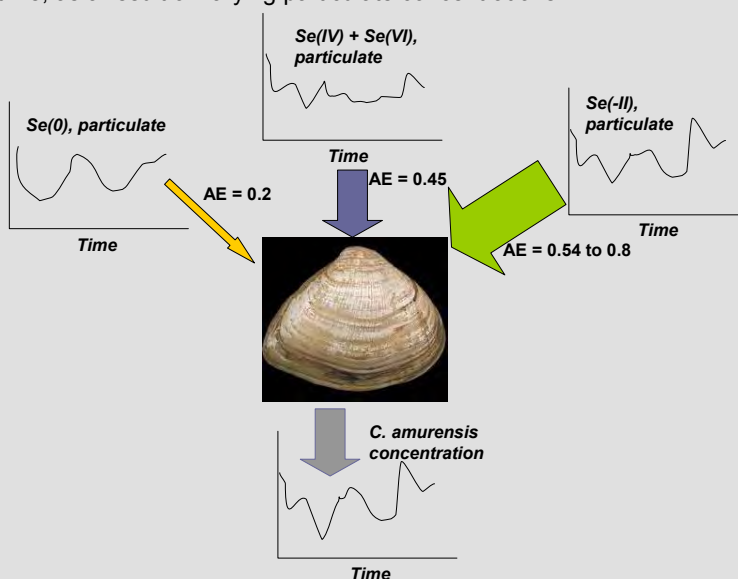
The DYMBAM approach has been found to predict selenium concentrations in clams (*Macoma balthica*) relatively well (Luoma et al., 1992). The use of this approach in predicting selenium concentrations in the mussel *Mytilus edulis* also show good agreement (Wang et al., 1996). Selenium concentrations in the bivalve *Corbula amurensis* were found to vary seasonally, with higher concentrations during low flow (Linville et al., 2002). Particulate selenium concentrations were also found to be higher during low flow. The linear relationship between selenium concentration in food and tissue concentrations as suggested in DYMBAM is considered as applicable in predicting selenium accumulation in this bivalve. Parameters for bioaccumulation of selenium through zooplankton were determined previously for NSFb as listed in the following table (Table 2-6).

Table 2-6
Parameters for DYMBAM Model for Zooplankton (Stewart et al. 2004)

Food Chain (species)	Ku (L/g/d)	IR (g/g/d)	AE (%)	Ke (d ⁻¹)	Tissue Se Concentration (mg/kg)	Reference
Mysid Copepods	0.024	0.42	50-53	0.155	0.7-2.2	Stewart et al. (2004)
N. Mercedis	0.027	0.45	73	0.25	0.9-2.7	Stewart et al. (2004)

Box 1. Selenium Uptake by Bivalves

In the model formulation, clams derive their selenium entirely from the different particulate phases, based on laboratory data that show minimal direct uptake of dissolved phase selenium (Luoma et al., 1992). Furthermore, the assimilation efficiency of uptake of particulate selenium varies by species. For *Corbula amurensis*, the species focused on in this work, laboratory data have shown that the highest efficiency of uptake is for selenium associated with algae or organic matter (present as selenides, or Se(-II)), and the lowest for particulate elemental selenium (Se(0)), with particulate inorganic selenium (Se(IV)+Se(VI)) efficiency somewhere in between (Schelkat et al., 2000, 2002; Lee et al., 2006). The model is set up to relate selenium uptake in clams to the simulated concentration of each of these particulate species as shown below. Clam concentrations can change over time, as a result of varying particulate concentrations.



2.7.1 Selenium Uptake by Higher Trophic Organisms

In NSFB, the most significant pathway of selenium bioaccumulation to the higher trophic level is through the benthic-feeding species. Building on the discussion presented in previous sections, the schematic of the processes leading to bioaccumulation in predator organisms is shown schematically in Figure 2-8. The primary organisms that fit this category are benthic-feeding fish, such as the white sturgeon (*Acipenser transmontanus*) and diving ducks (Lesser scaup, *Aythya affinis*; Greater scaup, *Aythya marila*; Surf scoter, *Melanitta perspicillata*). Concentrations in liver and muscle tissues of sturgeon and diving ducks have been measured in previous studies in the bay and in the San Joaquin Valley (White et al., 1987, 1988, 1989; Stewart et al. 2004; SFEI 2006).

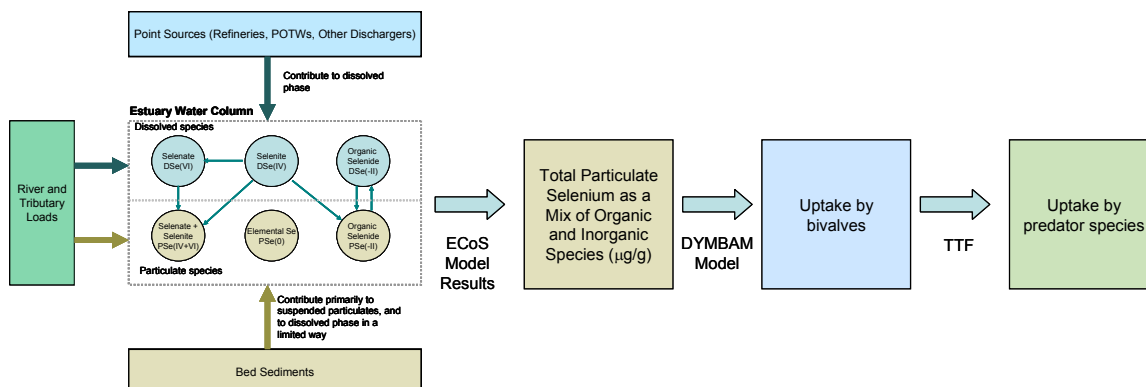


Figure 2-8 Schematic of selenium transfers from the water column and suspended particulates to bivalves, and then to predator species. The selenium sources and water column transformations are discussed in Sections 2.4, 2.5, and 2.6. Note that once selenium is bioaccumulated by bivalves, and present largely in the organic form, speciation is not a consideration in further uptake by predator species.

The transfer of selenium to higher trophic levels can be represented through relationships between dietary and tissue concentrations as measured in the field, or using exposures based on more general relationships between ingestion and body weight, or with literature estimates of trophic transfer factors (TTFs) which are ratios of diet concentrations to tissue concentrations. All three methods are described below.

2.7.2 Linear Relationships Using Field Data

Presser and Luoma (2006) developed linear relationships between concentrations in bivalves and predators (scaup, surf scoter, and sturgeon), using data sampled for the same location and time. Data for *C. amurensis* are lacking for years before 1995 and therefore concentrations for *Corbicula fluminea* for these years were used. For surf scoter and white sturgeon, derived linear relationships between tissue concentrations in *C. amurensis* and concentrations in predators are based on previous studies of Presser and Luoma (2006):

$$C_{surf} (liver) = 19.28 C_{mss} - 2.35 \quad (R^2 = 0.86) \quad (26)$$

$$C_{sturgeon} (liver) = 3.15 C_{mss} - 3.50 \quad (R^2 = 0.91) \quad (27)$$

$$C_{sturgeon} (flesh) = 1.68 C_{mss} + 1.04 \quad (R^2 = 0.66), \text{ Corbicula only} \quad (28)$$

where C_{mss} are concentrations in bivalves ($\mu\text{g/g}$), and C_{surf} (liver) and $C_{sturgeon}$ (liver) are concentrations in livers of surf scoter and white sturgeon. Equations for predicting concentrations in tissue were not reported for *C. amurensis*, and are shown only for *C. fluminea*. The relationship predicts a concentration of 209.7 $\mu\text{g/g-dwt}$ in surf scoter liver and 31.2 $\mu\text{g/g-dwt}$ in white sturgeon liver, given an average bivalve concentration of 11 $\mu\text{g/g}$ (Linville et al. 2002; Stewart et al. 2004). Data for selenium concentrations in surf scoter liver are lacking for recent years. Average concentration in white sturgeon liver is 24.1 $\mu\text{g/g-dwt}$ in the Bay, suggested by data collected by SFEI and USGS in 2000 and 2001. The linear relationships above are currently used in the model calculations.

2.7.3 Selenium exposures based on food ingestion

The exposure of a contaminant of potential ecological concern (COPEC) for birds and mammals can be calculated using pathway-specific exposure equations of the general form:

$$Exposure = \frac{EPC \times CR \times FC}{BW} \quad (29)$$

where:

EPC = exposure point concentration; the concentration of a COPEC in media that is likely to be contacted by receptors of concern.

CR = contact rates or intake rates; including ingestion and drinking rates.

FC = fraction of media contacted; including site presence index and diet portions.

BW = body weight of the receptor.

Exposure equations used in this approach are consistent with federal and state guidance (DTSC 1996a,b; U.S. EPA 1989b, 1993). The total exposure to each COPEC for birds was calculated as the sum of exposure via water ingestion, sediment ingestion, and the ingestion of food items. This can also be written as follows:

Exposure Dose = Exposure from water ingestion + Exposure from sediment ingestion + Exposure from food ingestion

Putting this equation in the form of the general equation given above for calculating exposure, the following equation is produced:

$$Exposure\ dose = \left[\frac{EPC_{water} \times DR \times FC}{BW} \right] + \left[\frac{EPC_{sediment} \times IR \times FC \times SPI}{BW} \right] + \left[\frac{EPC_{tissue} \times IR \times FC \times SPI}{BW} \right] \quad (30)$$

where:

EPC_{water} = EPC for a COPEC in water (in $\mu\text{g/L}$);

$EPC_{sediment}$ = EPC for a COPEC in sediment (in mg/kg);

- EPC_{tissue} = EPC for a COPEC in plant, invertebrate, or fish tissues (mg/kg);
- DR = Drinking, or surface water ingestion, rate (ml/day);
- IR = Ingestion rate of sediment or food (mg/day);
- FC = Fraction contacted (unitless; assumed to be 1);
- SPI = Site presence index (unitless; assumed to be 1); and
- BW = Body weight (kg).

Exposure factors were derived following the approach used by the Wildlife Exposure Factors handbook (U.S. EPA 1993), using primary literature sources.

The effects assessment identifies and quantifies potential adverse effects caused by exposures to the COPECs at the site and, where possible, evaluates cause-and-effect relationships (U.S. EPA 1992a). Potential adverse effects are quantitatively calculated as Hazard Quotients (HQs), which are estimated by dividing a receptor's exposure to a COPEC by the COPEC's TRV; i.e.,

$$HQ = \frac{Exposure}{TRV} \quad (31)$$

where:

- HQ = Hazard quotient
- TRV = Toxicity reference value

The toxicity reference value was based on a study of mallards performed by Heinz et al. (1989).

Allometric scaling factors were also used to adjust doses when the test species was not the same as the receptor species evaluated (Sample and Arenal 1999). These factors adjust for differences in body weight, metabolism, pharmacokinetics, and sensitivity to provide the best available estimates of species-specific toxicity.

The equation used for adjusting doses with allometric scaling factors is (Sample and Arenal 1999):

$$A_w = A_t \times \left(\frac{BW_t}{BW_w} \right)^{(1-b)} \quad (32)$$

Where:

- A_w = Toxicity value for a particular wildlife species;

- A_t = Toxicity value for the test species;
 BW_t = Body weight of the test species;
 BW_w = Body weight of wildlife species; and
 b = Allometric scaling factor provided by Sample and Arenal (1999).

Derived TRV values for three species: Surf Scoter, Greater and Lesser Scaup are shown in Table 2-7.

Table 2-7
Body Weight and TRV Values for Test and Wildlife Species

		Body Weight (kg)	Adjusted NOAEL-Equivalent TRV (mg/kg-day)		Source
			Low	High	
Test Species	Mallard Ducks	1.10	0.36	0.73	Heinz et al. 1989
			Allometrically Adjusted TRVs		
Wildlife Species	Surf Scoter	0.90	0.35	0.70	Calculated
	Greater Scaup	0.96	0.35	0.71	Calculated
	Lesser Scaup	0.79	0.34	0.68	Calculated

Hazard Quotients (HQs) are used to estimate the potential for adverse ecological impacts when exposure and toxicity data are available. An HQ is the ratio of the exposure to the TRV (mg/kg-day):

$$HQ = \frac{\text{Exposure}}{TRV} \quad (33)$$

An HQ less than 1 indicates that there is a negligible potential for adverse ecological impacts due to exposure to a particular COPEC, whereas an HQ greater than 1 indicates that there is a potential for adverse ecological impacts due to exposure to that COPEC. However, there are a number of conservative assumptions that are incorporated in the estimated HQs and a value slightly greater than 1 does not indicate significant risk. The conservative assumptions include the consumption only of *Corbula amurensis* (i.e., the diet items with the highest selenium content), the presence of the birds in the bay 100% of the time, and using time series values of dietary concentrations, with periods of high concentrations not averaged out.

For birds and mammals, both NOAEL TRVs and LOAEL TRVs were derived, and were used to calculate corresponding NOAEL HQs and LOAEL HQs. A NOAEL HQ gives a conservative estimate of the comparison between exposure at site conditions and maximum safe exposure levels. A NOAEL HQ less than 1 would indicate that no risks are likely to occur from that particular exposure. The LOAEL HQ represents a comparison of exposure

at site conditions with doses known to result in effects. A LOAEL HQ greater than or equal to 1 would indicate that a potential for risks exists. If the NOAEL HQ is greater than or equal to 1, and the LOAEL HQ is less than 1, a conclusion must be drawn by close evaluation of several factors (e.g., exposure parameters, magnitude of the HQ, source of the TRV, probability of site use by the receptor, and special-status of the receptor).

2.7.4 Trophic Transfer Factors

Recent compilation of data suggests that there is a relatively well defined relationship between concentrations of selenium in organism diets and in their tissues (Presser and Luoma, personal communication, 2009, manuscript under development). A ratio between selenium concentrations in tissue and diet of organisms, Trophic Transfer Factor (TTF) can be used in estimating bioaccumulation of selenium through the food web, once dietary concentrations are known. The ratio can be derived based on kinetic uptake rates or observed concentrations of diet and tissue. For example, TTF for invertebrates can be derived as: $TTF = (AE)(IR)/k_e$, where AE = assimilation efficiency; IR = Ingestion rate, and k_e = elimination rate. For most fish species the TTF ranges from 0.9 to 1.1, although higher values of 1.7 have been reported for one data set with white sturgeon. TTFs have also been found to vary with ambient selenium concentration. For the purpose of this calculation, TTFs of 1.1 and 1.7 for white sturgeon are both used. A TTF of 1.8 has been reported for scaup in the estuary from a diet primarily of *C. amurensis* (Presser and Luoma, personal communication, 2009).

2.8. SUMMARY OF MODEL FORMULATION

The combined set of equations used to represent selenium fate and transport, including ancillary parameters such as salinity, suspended solids, phytoplankton, and uptake by clams and predator species is presented in summary form in Box 2. As noted above, the basic equations used in this work are those of Meseck and Cutter (2006), with additions for biological uptake.

Box 2. Model Equations

2.9. BOUNDARY CONDITIONS AND EXTERNAL LOAD INPUTS

The definition of boundary conditions is a key step in the solution of the set of coupled differential equations discussed above, and has a major impact on the concentrations of different species that are calculated (see Box 3). This section presents the rationale for the boundary conditions used in this application, which occur primarily at the freshwater and seawater ends. Also related to this definition are the external loads that are added to the estuary in the form of other point sources, local tributary inputs, or input from the South Bay as shown schematically in Figure 2-9.

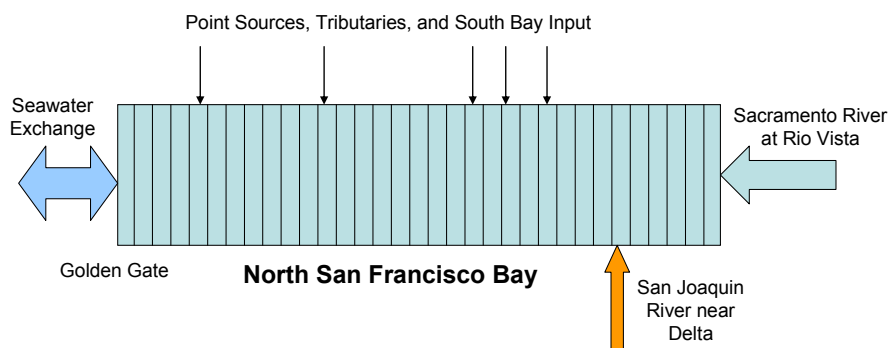
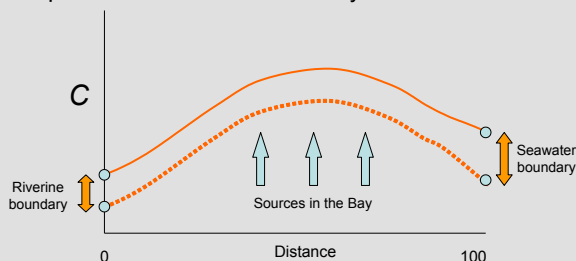


Figure 2-9 Schematic of model representation of the NSFB, showing model cells or nodes (vertical boxes), boundary conditions, and external loads. Each cell is 3 km wide. The locations of the external loads are illustrative, and are added in the model location at the approximate location they enter the estuary.

Box 3. Boundary Conditions

Differential equations represent change in space and/or time, and the solution of any differential equation requires the definition of initial and boundary values. In the context of the 1-D simulation of various concentrations over distance through the NSFB, and over time, this refers to initial values of all constituents through the length of the estuary, and concentrations at the freshwater and seawater ends. Together with other inputs along the length of the estuary, such as point sources, local tributaries, and sources from the South Bay, these define the calculated concentrations along the estuary, as shown below. Even when other parameters in the equations stay the same, the boundary conditions can determine the concentrations in the estuary. For this reason, it is important to get an accurate representation of the boundary values, and when these are not well known, to consider a range of values to represent possible conditions in the bay.



In ECoS3, three types of boundary conditions can be specified: closed boundary, open boundary with a set value (boundary concentration) and open boundary with a gradient. An open boundary condition (with seawater end member concentration) is usually used for the estuary mouth. The riverine boundary condition can be specified either as closed boundary or open boundary. When modeled using open boundary, a riverine endmember concentration is needed. In this application, all the solutes except salinity were modeled using a closed riverine boundary condition, with riverine inputs (loads) specified as riverine concentrations multiplied by flow.

Boundary conditions need to be defined for the calibration year (1999), as well as for all years of the simulation, typically 1999-2006 for this application. Boundary conditions were generally defined by measurements for 1999, and either by measurements or through assumptions for subsequent years.

2.9.1 Flow

The riverine flow boundary used is the flow record at the Sacramento River at Rio Vista, obtained from DAYFLOW record from Interagency Ecological Program (IEP; <http://www.iep.ca.gov/dayflow/index.html>). The San Joaquin River is modeled as a tributary to the estuary, with flow derived as the difference between Net Delta Outflow Index (NDOI) and flow from the Sacramento River at Rio Vista. Figure 2-10 shows the time series of daily outflow from Delta, Sacramento River at Rio Vista and estimated San Joaquin River flow input. Another freshwater input is the direct precipitation on water surface of the bay. Precipitation data were obtained from the California Irrigation Management Information System (CIMIS) for a station near Napa (Station #109). Locations for CIMIS stations around the Bay area are shown in the Appendix (Figure A.4-1). Evaporation loss from the water surface was estimated based on values from Uncles and Peterson (1996) and ranged between 0.95×10^{-8} m/s in December to 6.2×10^{-8} m/s in July.

Simulations presented in this work depend on data availability, but in most cases are for the years 1999 to 2006. There are some exceptions when data are shown for years preceding 1999; this is largely to demonstrate model performance in under different hydrologic regimes. A more complete summary of the inflows from the Sacramento and San Joaquin River watersheds to the Delta, and the hydrologic classification of the water years by the California Department of Water Resources is shown in Figure 2-11.

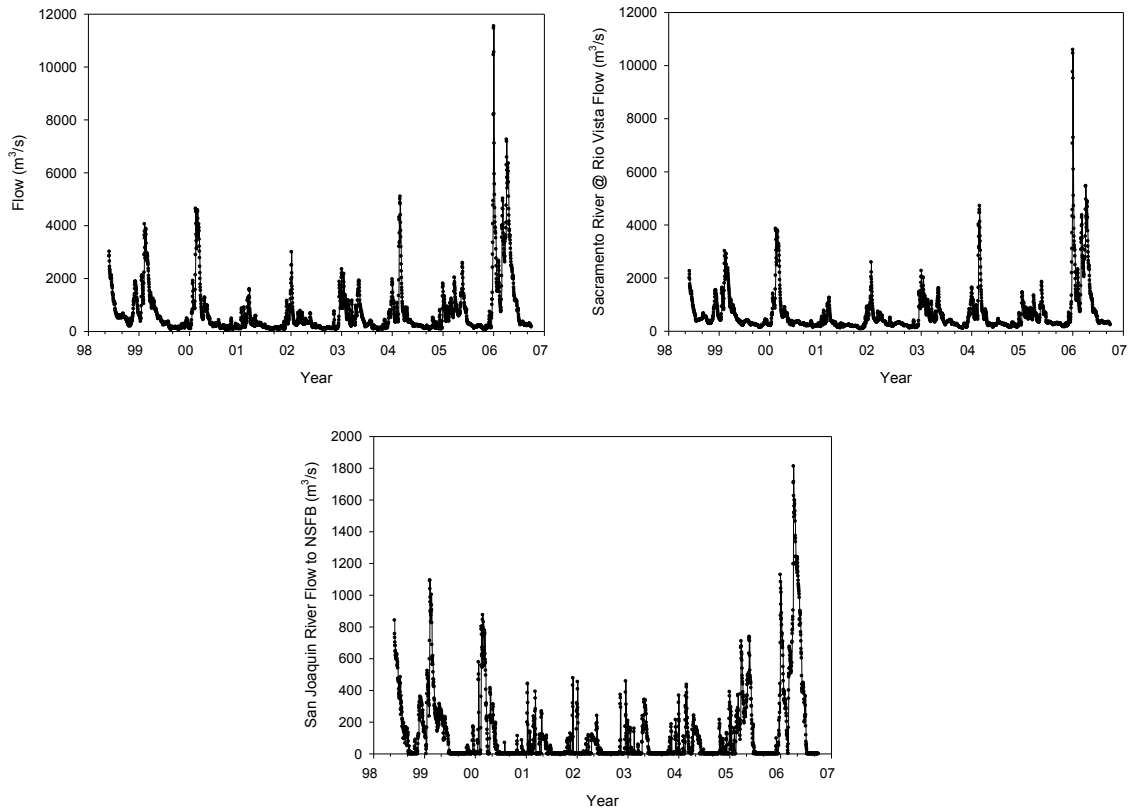


Figure 2-10 Daily outflow from (a) Delta, (b) Sacramento River at Rio Vista, and (c) San Joaquin River. (Data source: IEP) Note that the y-axis values for San Joaquin River are different, and that during the dry periods of most years, the contribution of San Joaquin River flow to the bay is practically zero.

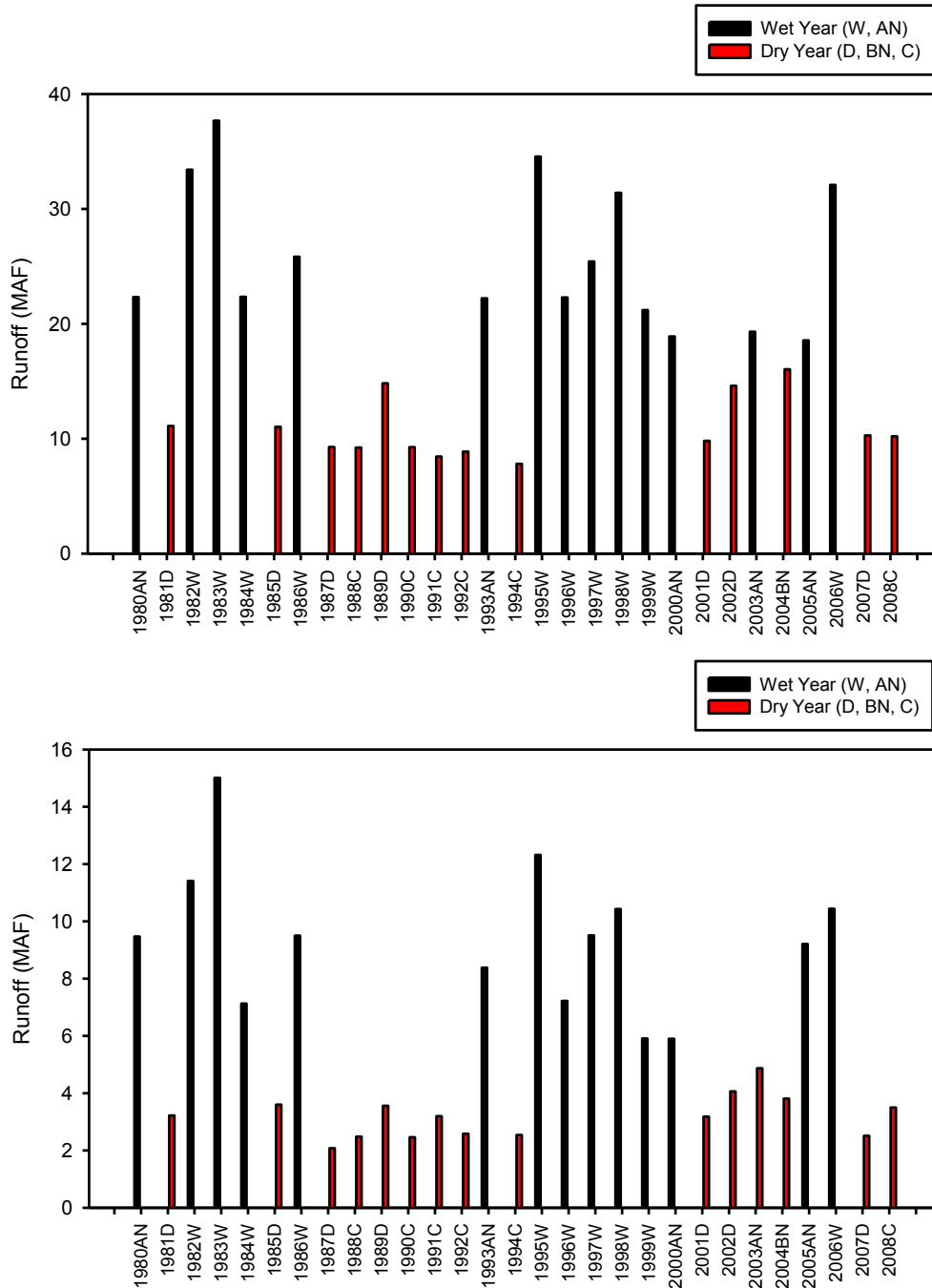


Figure 2-11 Annual flow from the Sacramento and San Joaquin River basins and the hydrologic classification by the California Department of Water Resources.

2.9.2 Total Suspended Material (TSM)

The seawater end member of TSM was specified to be 0.01 g/L and was held constant over the duration of the simulation period.

Riverine inputs of TSM loads were modeled as riverine flow multiplied by concentration, with PSP and BEPS as a fraction of TSM, as in the newest routine of ECoS3 (v3.39; Harris

and Gorley, 1998). Concentrations of TSM from rivers are modeled as a function of river flow, with higher sediment concentrations occurring under high flow (Harris et al. 1984):

$$TSM_{river} = a + b * Q_{sac}^c \quad (34)$$

where a is the minimum concentration in the river water, and b and c are calibration coefficients. TSM concentrations derived from the above equation compared to the observed concentrations at Rio Vista are shown in Figure 2-12. ($r = 0.312$). The riverine inputs of TSM loads are derived from flow multiplied by concentrations (Figure 2-13).

The inputs of TSM from the San Joaquin River were modeled as a separate source, with concentrations derived from the equation above based on flow from the San Joaquin River (Figure 2-9) and loads derived from flow multiplied by concentrations (Figure 2-13). The inputs from San Joaquin River were added at the location where San Joaquin River flow enters the estuary ($X = 19$ km). Note that this approach uses the best representation of TSM data from San Joaquin River near the confluence with the estuary, and these concentrations are different from values upstream at Vernalis, where the San Joaquin River enters the Delta.

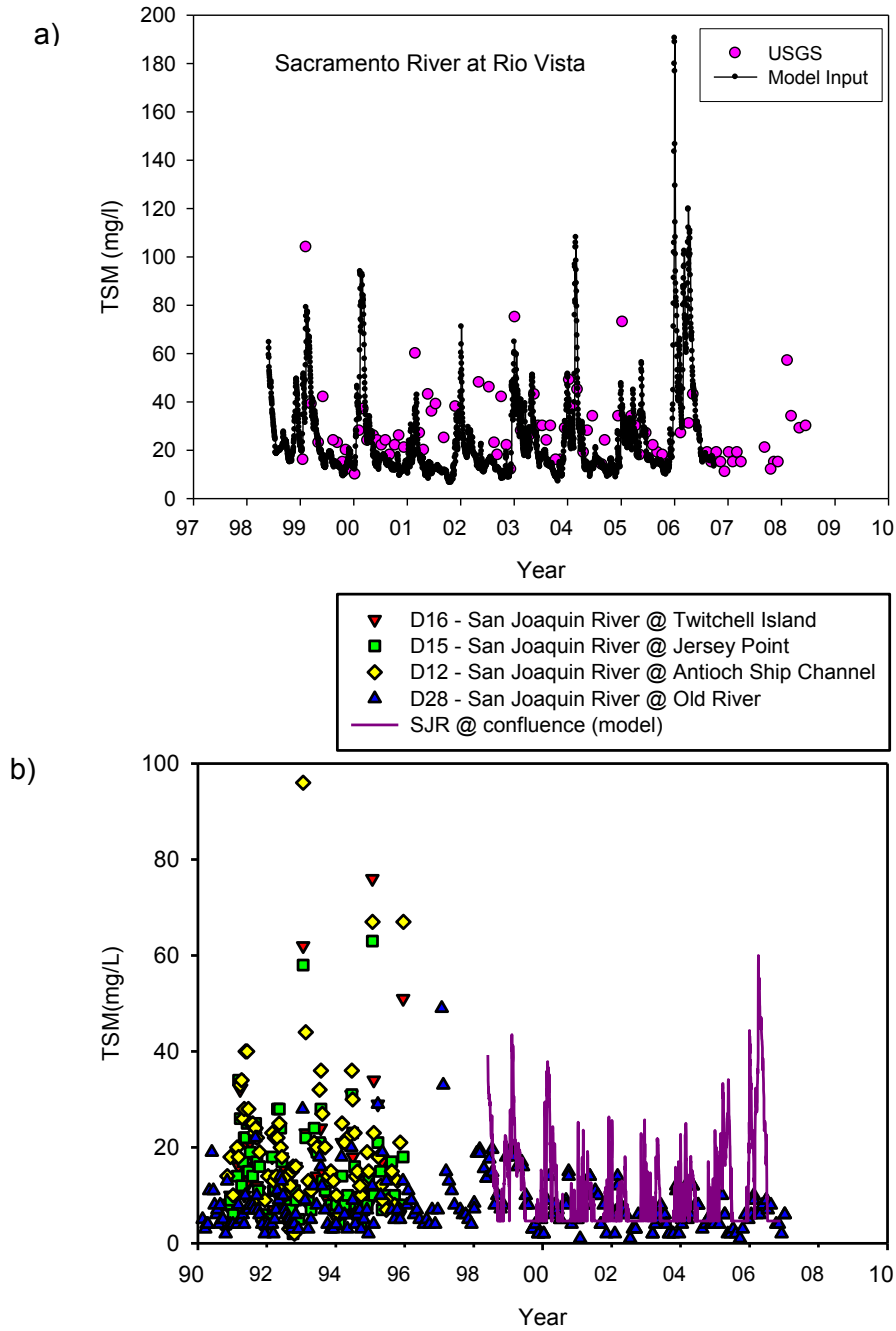


Figure 2-12. Model inputs of TSM concentrations for (a) Sacramento River at Rio Vista and (b) San Joaquin River at confluence compared to observed values (Data source: USGS). The stations shown for San Joaquin River are in the Delta, downstream of Vernalis.

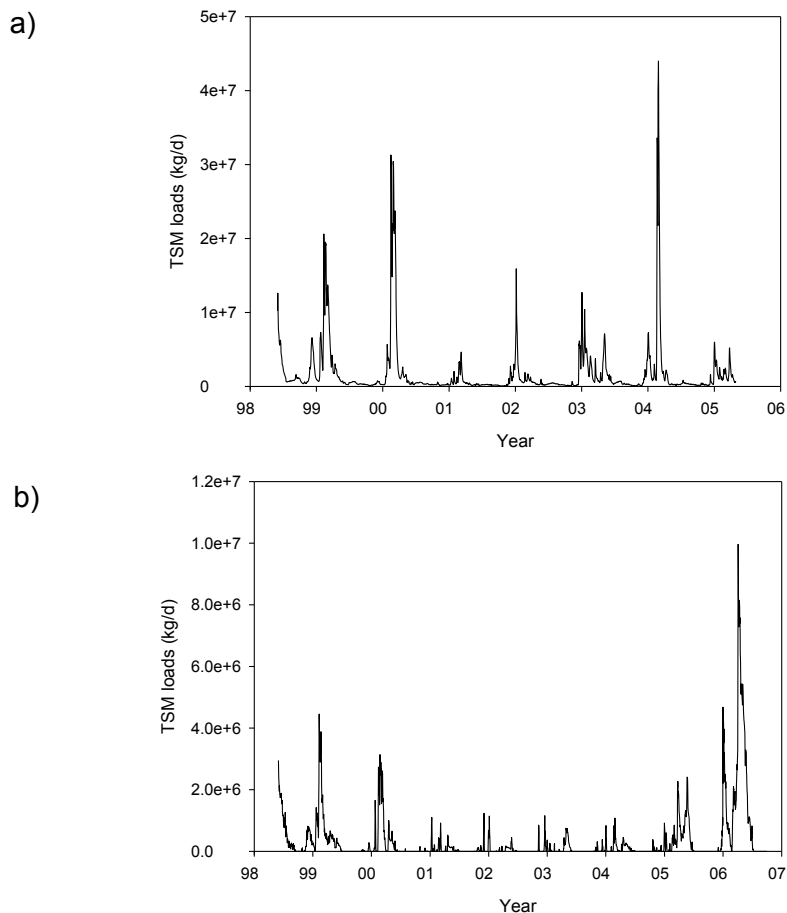


Figure 2-13 Model inputs of riverine loads of TSM for (a) Sacramento River at Rio Vista and (b) San Joaquin River at confluence (Data source: USGS). Note that y-axis values of TSM loads are about an order of magnitude lower for San Joaquin River compared to Sacramento River.

2.9.3 Phytoplankton

The riverine inputs of phytoplankton were specified as flow multiplied by time series chlorophyll a concentration data, for inputs from the Sacramento and San Joaquin Rivers. For the principal riverine input on Sacramento River at Rio Vista, data were reported on roughly a monthly basis. Data were obtained from the Bay Delta and Tributaries (BDAT) project site (<http://bdat.ca.gov/index.html>) and the USGS for the Sacramento River at Rio Vista as shown in Figure 2-14. Chlorophyll a concentrations were relatively high during 2002-2004. Riverine loads of phytoplankton from Sacramento River at Rio Vista are shown in Figure 2-15. Chlorophyll a concentration data from San Joaquin River at Twitchell Island obtained from BDAT multiplied by flow were used as San Joaquin River input (Figure 2-14). Inputs from the San Joaquin River were added as a point source at a location of $X = 19,000\text{m}$.

The seawater concentration was set at $2.3 \mu\text{g Chl a/L}$ as suggested in data from Cutter and Cutter (2004).

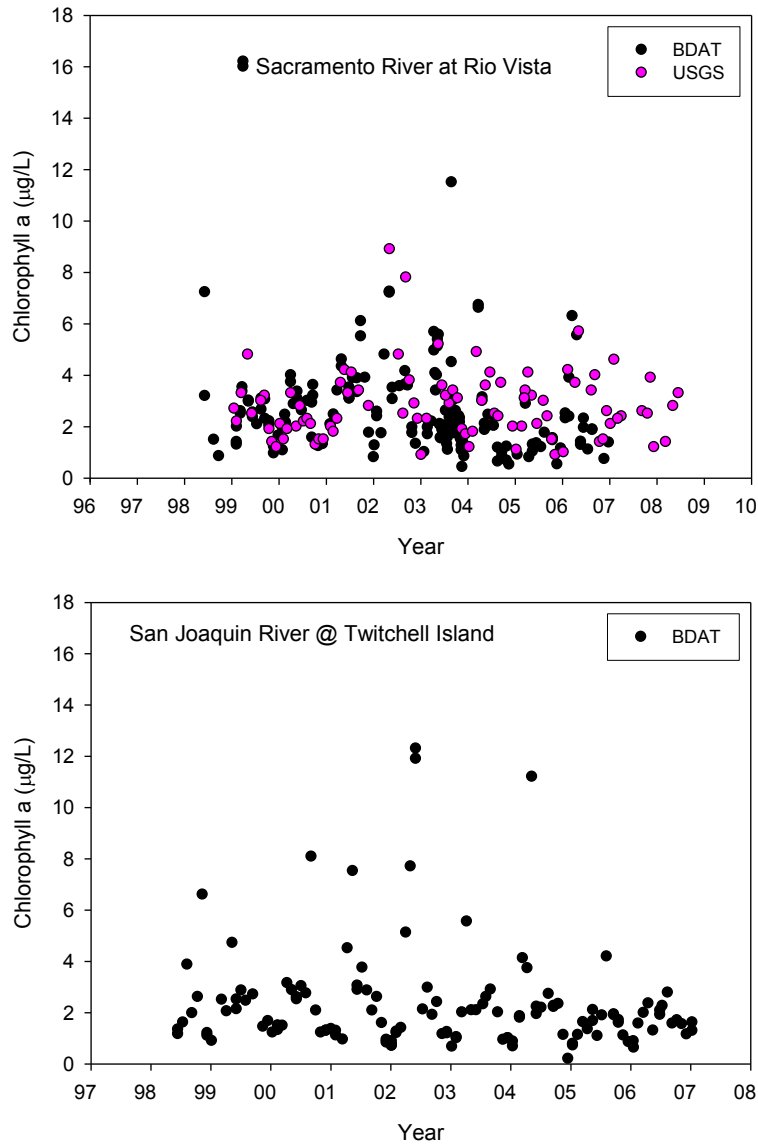


Figure 2-14 Chlorophyll a concentrations at the head of the estuary in the Sacramento River at Rio Vista and in San Joaquin River at Twitchell Island (Data source: BDAT, USGS).

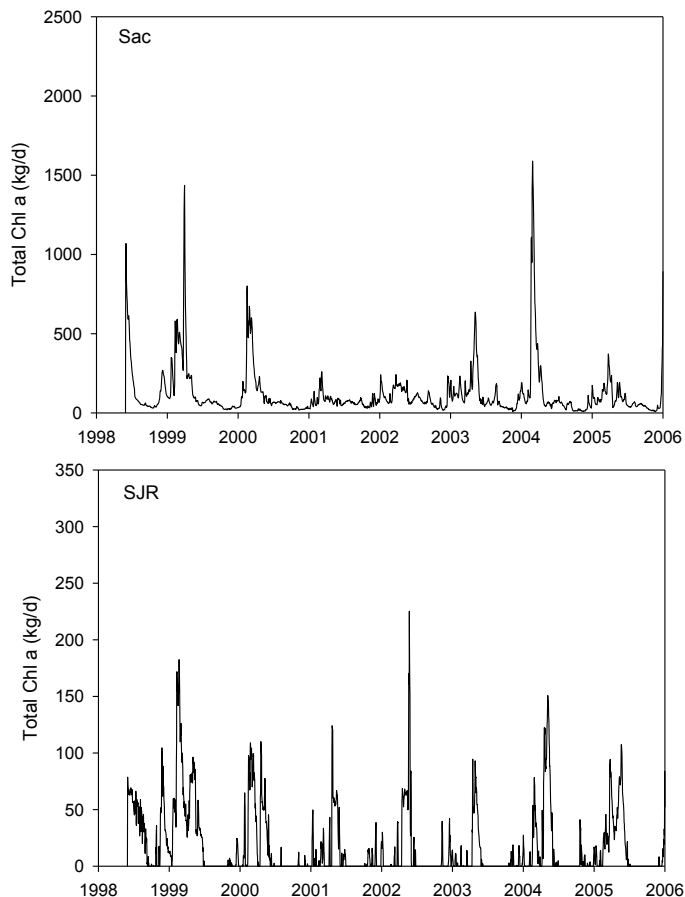


Figure 2-15 Riverine chlorophyll a loads at the head of the estuary in the Sacramento River at Rio Vista and San Joaquin River at confluence (Data source: BDAT, USGS).

2.9.4 Dissolved Selenium

The seawater end member of dissolved selenium was set at 1 nmol/L or 0.0789 $\mu\text{g/L}$ (Cutter and Bruland, 1984).

Dissolved selenium inputs for selenate, selenite, and organic selenide were specified from the rivers as follows:

- **Sacramento River:** Selenium concentrations for each species from Sacramento River at Rio Vista multiplied by flow at Rio Vista.
- **San Joaquin River:** Selenium concentrations from San Joaquin River at Vernalis reduced by species-specific Delta removal constants, multiplied by flow from San Joaquin River at confluence (Figure 2-8). The Delta removal constants reflect loss of selenium in the Delta and export through aqueducts. The removal constants are parameters that are derived through the model calibration and were 0.74 for selenate, 0.67 for selenite, and 0.47 for selenide. Inputs from the San Joaquin River were added to the model at a location of $X = 19$ km. The approach used to define the input concentrations in the model are shown in Figure 2-16.

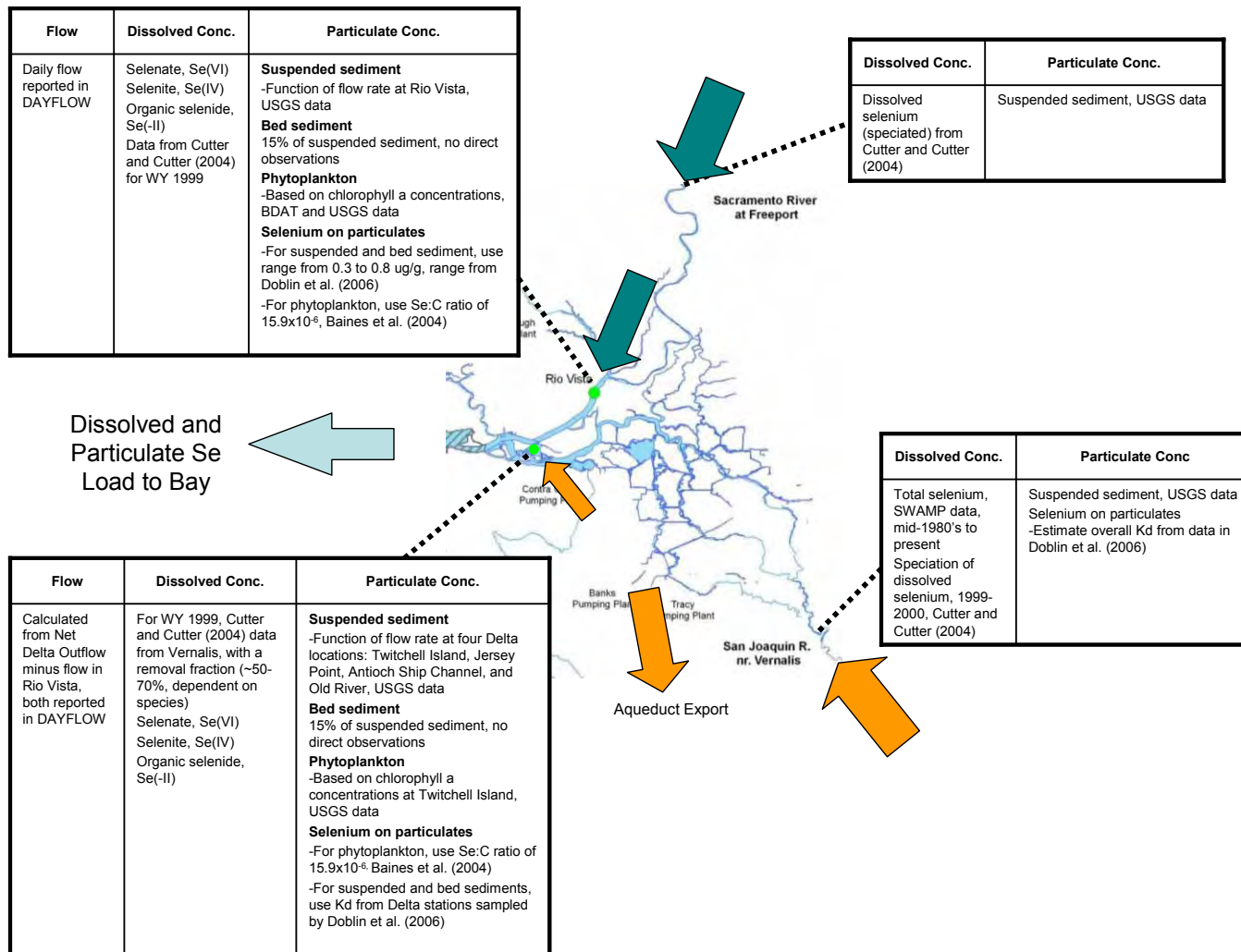


Figure 2-16 Concentrations of selenium, dissolved and particulate, by species, for the Sacramento and San Joaquin Rivers. Flows measured or estimated at related locations (Freeport, Rio Vista, Vernalis, and the confluence of San Joaquin River with Sacramento River) are used to estimate loads that define the upper boundary of the model at Rio Vista. Selenium from San Joaquin River is added as a load (flow times concentration, by species) 19 km downstream of Rio Vista. The entire load from Vernalis does not reach the Bay because of uptake/settling in the Delta, as well as because of water export through the aqueducts.

Concentrations of different species of dissolved selenium from Sacramento River at Freeport and San Joaquin River at Vernalis were simulated using the following general fitting equation, to account for dates for which measurements are not available:

$$y = y_o + a_o * \sin\left(\frac{2 * \pi * T}{b_o} + c_o\right) \quad (35)$$

where y_o is the initial selenium concentration ($\mu\text{g/L}$) at when $T = 0$, a_o ($\mu\text{g/L}$), b_o , and c_o are fitting constants, π is the constant 3.1416, and T is the time in Julian days. Parameters for y_o , a_o , b_o , and c_o for three dissolved selenium species were derived based on measured concentrations at Sacramento River at Rio Vista and San Joaquin River at Vernalis as listed in Table 2-8. Selenium concentrations measured in the rivers are mainly for the year of 1998-2000. Measured and fitted concentrations for different species of selenium are shown in Figure 2-17 and Figure 2-18. The best fit parameters from the data were used to extrapolate concentrations for the simulation period of 1999-2006. These were multiplied by flow to estimate loads. Estimated daily dissolved selenium loads from the Sacramento River (at Rio Vista) and San Joaquin River (at the confluence) by different species are shown in Figure 2-19.

In a previous memo (TM2, Tetra Tech, 2008a), the relative contribution of dissolved selenium loads to the Bay from the Sacramento River and San Joaquin River was estimated using a slightly different set of assumptions. The TM-2 method used daily flow and monthly concentrations at Freeport to estimate loads from the Sacramento River. The San Joaquin River loads were estimated as daily flow multiplied by daily concentrations derived from a flow-concentration relationship at Vernalis and a delta removal constant of 0.6, as in Meseck (2002). Estimated annual dissolved selenium loads from the two rivers using these two methods (TM2 and the current model application) are similar (Figure 2-20), except for 2006 which was a very wet year. For the Sacramento River, the model used selenium concentrations at Freeport multiplied by flow at Rio Vista. This results in similar estimates of selenium loads from Sacramento River to the TM-2 estimates. For the San Joaquin River, the model used selenium concentrations at Vernalis multiplied by flow at the confluence and a calibrated removal constant (species-specific, listed in Table 3-3). The estimated loads used in the model are slightly lower than TM-2 estimates for dry years, although broadly comparable.

Table 2-8
Constants for Simulating Species of Dissolved Selenium for the Sacramento and San Joaquin River (after Meseck, 2002)

	a_o ($\mu\text{g/L}$)	b_o	c_o	y_o ($\mu\text{g/L}$)	r
Sacramento River					
Selenite	0.016	75	0.41	0.022	0.69
Selenate	0.132	1556	3.77	0.503	0.44
Organic selenide	0.111	312	1.32	0.217	0.13
San Joaquin River					
Selenite	0.002	125	4.87	0.007	0.62
Selenate	0.023	622	5.30	0.047	0.57
Organic selenide	0.009	76	5.49	0.027	0.69

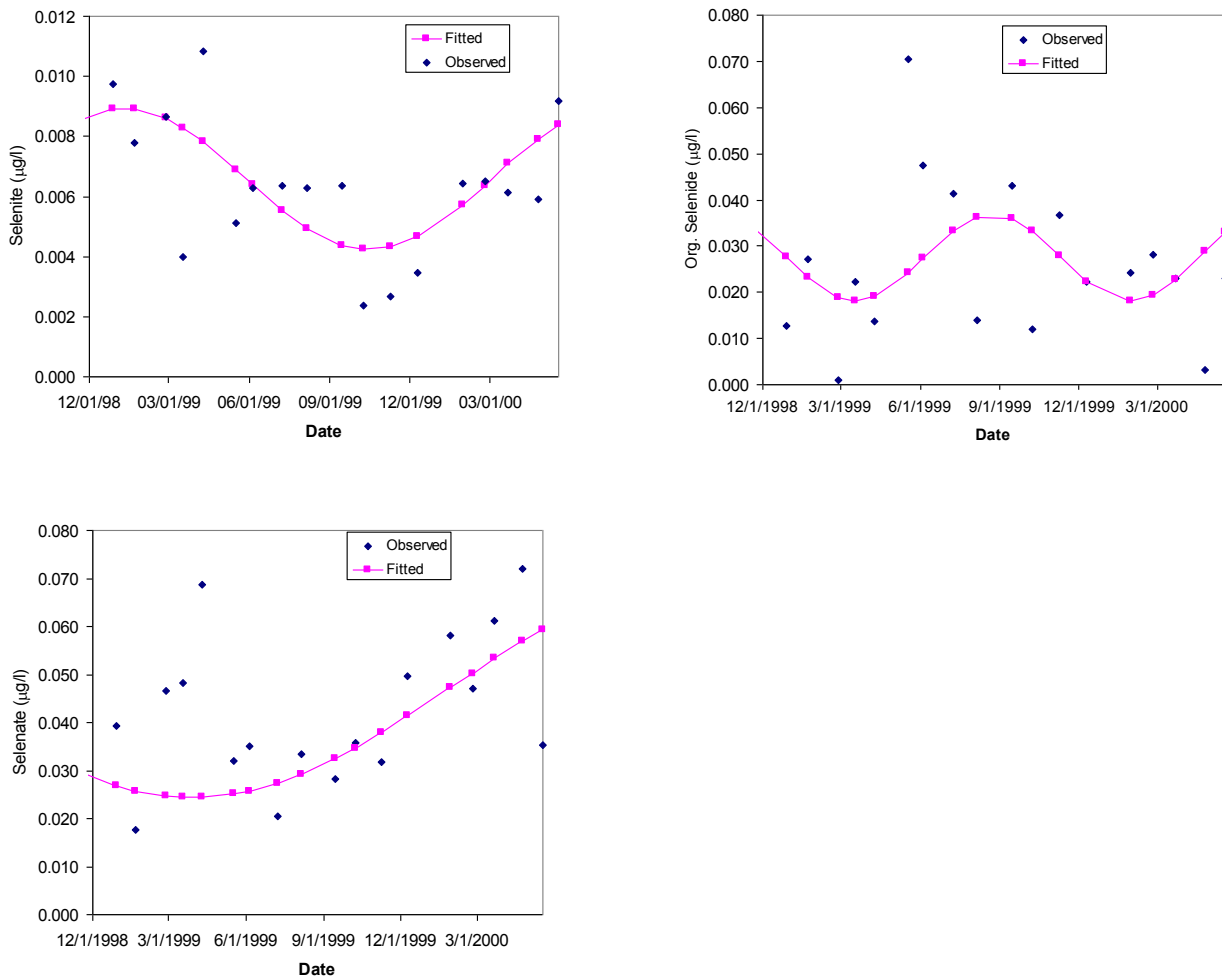


Figure 2-17 Fitted dissolved selenium concentrations compared to observed concentrations from the Sacramento River at Rio Vista (Data source: Cutter and Cutter, 2004).

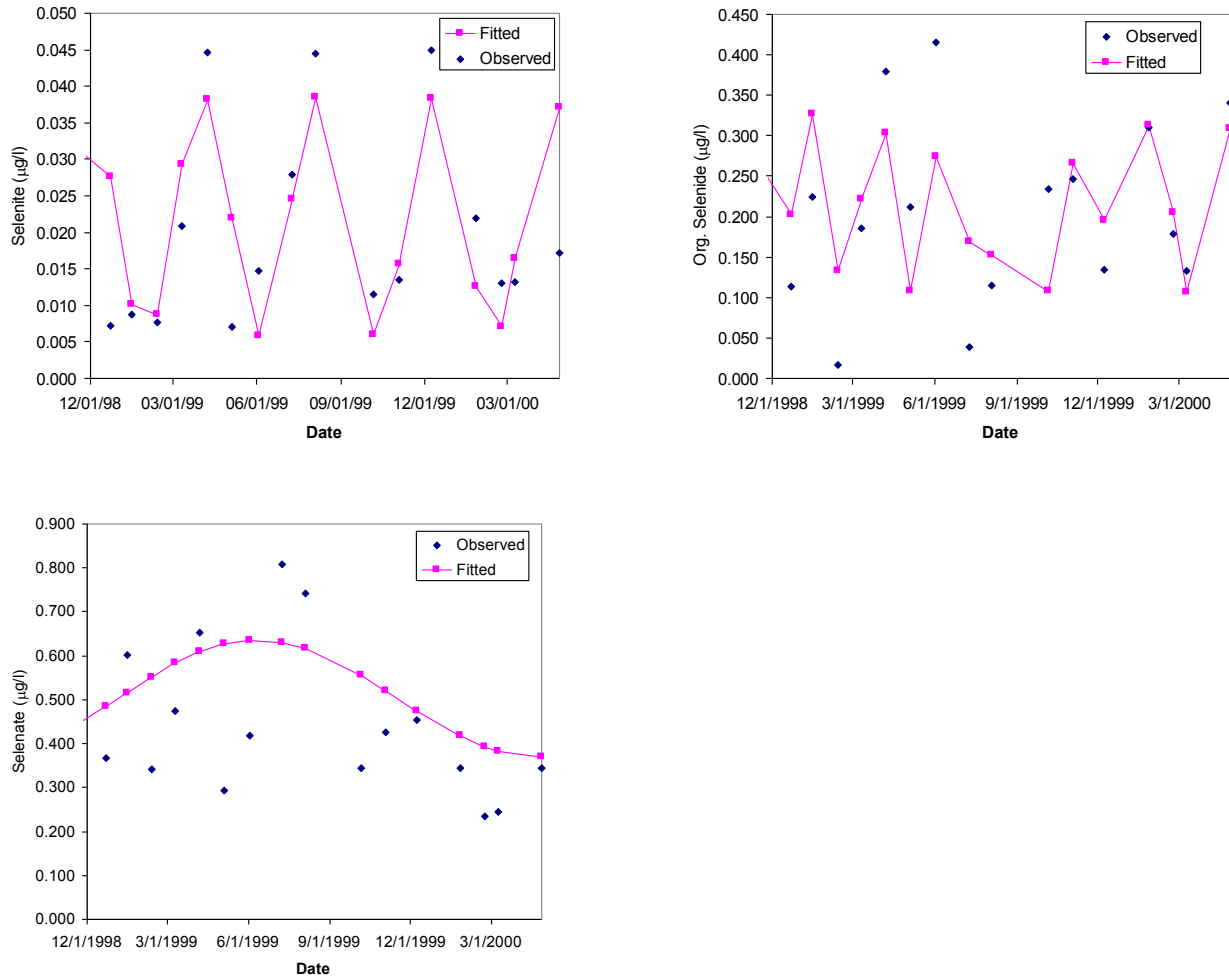


Figure 2-18 Fitted dissolved selenium concentrations compared to observed concentrations from the San Joaquin River at Vernalis (Data source: Cutter and Cutter, 2004).

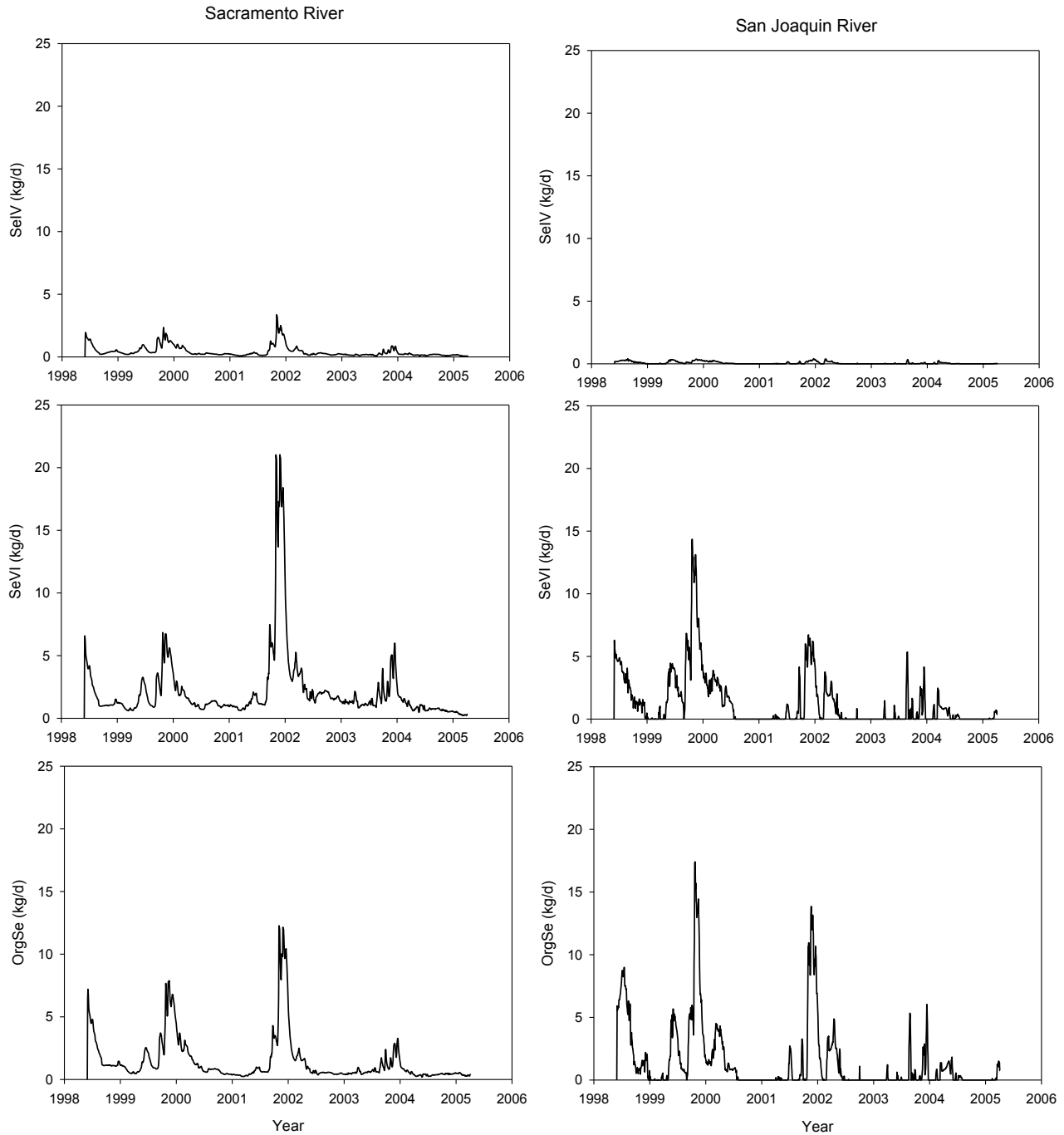


Figure 2-19 Riverine inputs of different species of dissolved selenium from the Sacramento River at Rio Vista and the San Joaquin River at the confluence. Selenium concentrations underlying these load estimates were mainly for the years 1998-2000 and 1984-1988. During the 20 year period, selenium concentrations from the Sacramento River remain relatively constant (Cutter and Cutter, 2004).

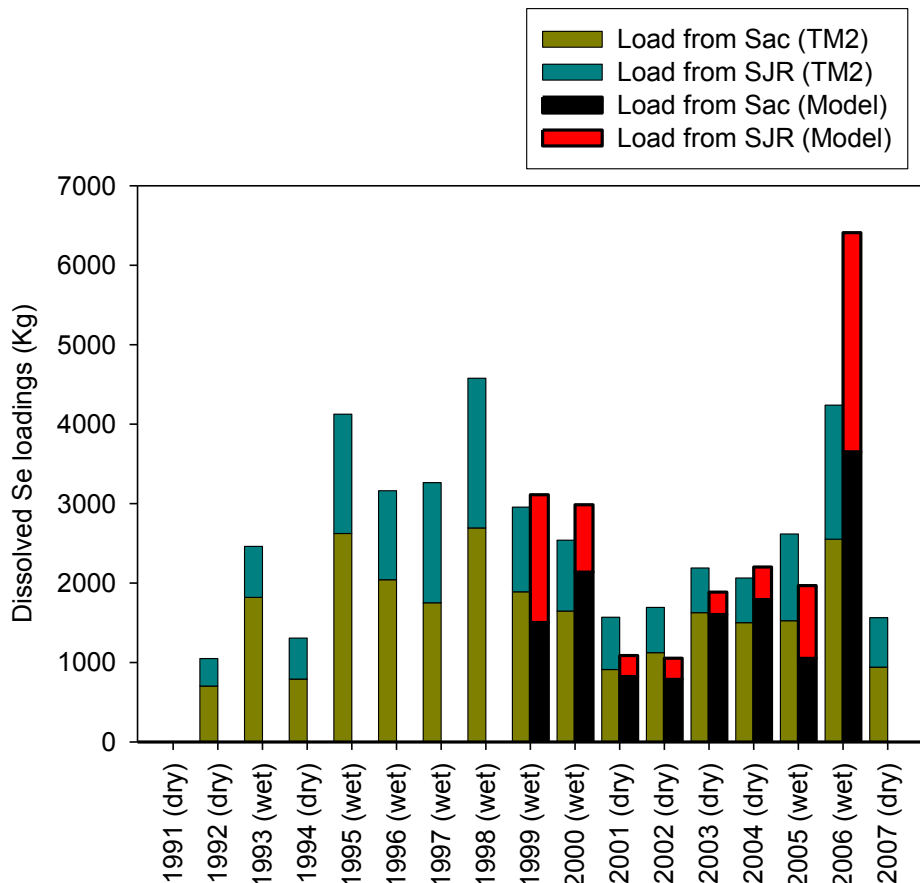


Figure 2-20 Dissolved selenium loads from Sacramento River and San Joaquin River to the Bay estimated in TM2 and in the model (the load estimates were based on concentrations between 1998-2000).

Daily selenium loads from local tributaries estimated in a previous technical memo by Tetra Tech (Tetra Tech, 2008a) were added to the model using the annual load for each hydrological area multiplied by a time series scaling factor, derived from daily flow record at Napa River (USGS11458000; Figure 2-21). No speciation data exist for local tributaries. The speciation from local tributaries is assumed to be the same as from the Sacramento River reported by Cutter and Cutter (2004): selenite (9%), organic selenide (35%) and selenate (56%). The total selenium load from tributaries estimated in the model varies depending on the volume of runoff each year, and was 819.7 kg/yr for 1999.

Daily refinery loads over 1999-2006 from five refineries in the NSFB estimated in Tetra Tech (2008a) were used in the model calibration, with speciation held constant at values reported by Cutter and Cutter (2004): selenite (13%), organic selenide (30%) and selenate (57%). The daily loads varied from day to day depending on the effluent data reported, and was 558.8 kg/yr for 1999.

A time series of refinery and tributary selenium loads is shown in Figure 2-22. The tributary loads were significant during the high flow season and minimal during the remainder of the year. Refinery loads are relatively constant throughout the year.

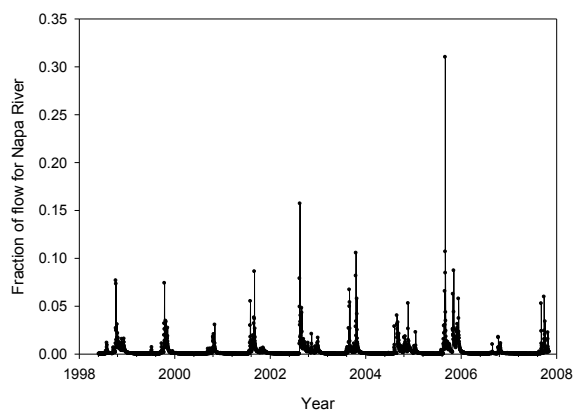


Figure 2-21 Flow as a fraction of mean annual flow at Napa River

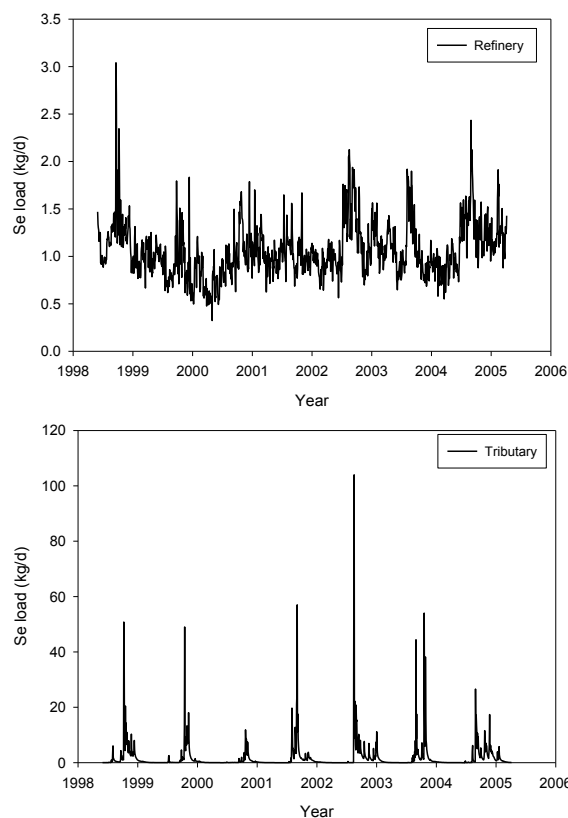


Figure 2-22 Daily refinery and tributary inputs of dissolved selenium

Selenium loads from other point sources including municipal and industrial wastewater discharges were also added to the model (Table 2-9). Speciation for municipal wastewater discharges used is organic selenide (15%), selenite (25%), and selenate (60%). The locations where selenium loads from point sources and tributaries were added to the estuary are also listed in Table 2-9. For these sources, the loading was specified as an average daily value for the entire period of the simulation because there was insufficient data from all dischargers to estimate load variability over 1999-2006. For 1999, the total loads from these POTWs sources were 175.8 kg/yr.

Table 2-9
Selenium Loads from Point Sources and Tributaries

Number	Point Source Name	Type	Distance from Head (km)	Daily Load (kg/d)
1	San Rafael	Tributary	80.9	0.207*
2	Berkeley	Tributary	87.9	0.103*
3	San Francisco Bayside	Tributary	95.1	0.037*
4	Novato	Tributary	70.9	0.155*
5	Petaluma River	Tributary	68.9	0.177*
6	Sonoma Creek	Tributary	65.5	0.188*
7	Napa River	Tributary	55.1	0.530*
8	Pinole	Tributary	72.6	0.127*
9	Fairfield	Tributary	36.8	0.367*
10	Concord	Tributary	41.2	0.407*
11	Tesoro	Refinery	42.1	0.19
12	Valero	Refinery	44.1	0.2
13	Shell	Refinery	45.9	0.59
14	ConocoPhillips	Refinery	59.2	0.16
15	Chevron	Refinery	76.8	0.33
16	City of American Canyon	Municipal	56.0	0.008
17	City of Benicia	Municipal	46.8	0.010
18	Central Contra Costa	Municipal	41.1	0.060
19	Central Marin	Municipal	8.0	0.034
20	Delta Diablo	Municipal	19.3	0.177
21	EBMUD	Municipal	98.9	0.095
22	Fairfield Suisun Sewer	Municipal	37.8	0.052
23	Las Gallinas	Municipal	74.0	0.009
24	Mount View	Municipal	44.3	0.006
25	Napa S.D.	Municipal	56.0	0.011
26	City of Petaluma	Municipal	71.6	0.019
27	Cities of Pinole and Hercules	Municipal	58.4	0.011
28	Rodeo	Municipal	59.0	0.002
29	Sausalito-Marin	Municipal	95.4	0.015
30	US Navy Treasure Island	Municipal	96.0	0.001
31	Vallejo Sanitation	Municipal	54.5	0.056
32	West County Agency WCA	Municipal	84.9	0.092
33	Rhodia Basic Chemical	Industrial	43.5	0.004
34	Dow Chemical	Industrial	20.7	0.006
35	General Chemical	Industrial	29.7	0.005
36	GWF (I)	Industrial	26.1	0.001
37	GWF (V)	Industrial	31.9	0.0004
38	USS-Posco	Industrial	20.1	0.031

*tributary loads are highly variable; the loads shown are mean daily loads.

Box 4. San Joaquin River Concentrations and Loads at Vernalis

The selenium loads from the San Joaquin River enter the Delta at Vernalis and are used as an input to the model. The Vernalis concentrations are attenuated by a removal constant before delivery to the NSFB, reflecting transformation/settling processes, as well as export in the aqueducts. Total selenium concentrations at Vernalis have been monitored at a relatively high frequency for more than two decades through the State of California's SWAMP monitoring program, and show a decline from values in the 1980s (Figure A below). Also, as discussed in the text, speciation data on selenium at Vernalis in 1999 have been reported by Cutter and Cutter (2004).

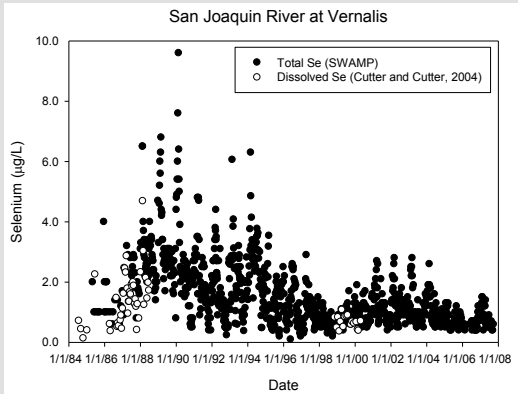


Figure A: Selenium data from Vernalis. The Cutter and Cutter (2004) data are for dissolved selenium, and the SWAMP data are for total (dissolved plus particulate) selenium.

For the model input, the speciated data for 1999, fitted with the trigonometric functions described in the text, was used to extrapolate concentrations over 1999-2006 in Vernalis. These concentrations were multiplied by the Delta removal constant for each species, and multiplied by flow at the San Joaquin river confluence to compute loads by species.

An alternative approach would be to use the total selenium data from SWAMP over 1999-2006, the ratios of selenium species from the Cutter and Cutter (2004) work, and the Delta removal constants to calculate loads delivered to the bay. The load estimation using the two approaches is compared in Figure B. For most years of the simulation, the two load estimation methods compare well. An exception is for 2006, which is a high flow year, where the SWAMP data approach resulted in a larger load estimate than the Cutter and Cutter (2004) data approach.

For model simulations over 1999-2006 presented in this work the Cutter and Cutter (2004) data-derived loads are used because of the speciation information. However, for simulations in years preceding 1999, the SWAMP data may be used.

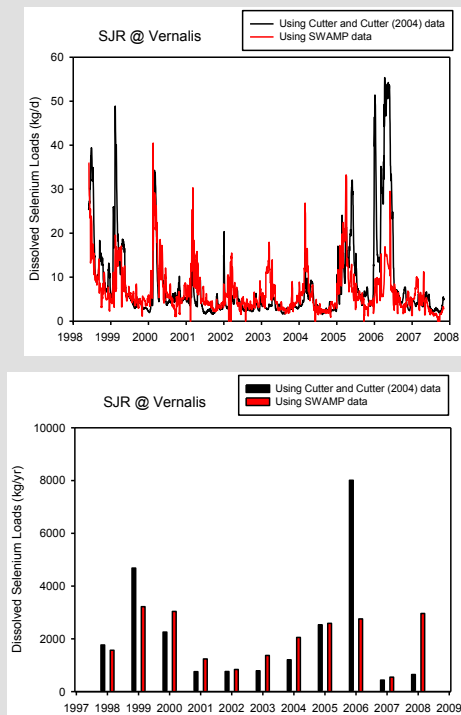


Figure B: Estimated selenium loads on a daily and a water year basis at Vernalis, computed using the Cutter and Cutter (2004) data and using the SWAMP data.

2.9.5 Particulate Selenium

Riverine particulate selenium inputs are estimated as selenium concentrations associated with PSP and BEPS (in $\mu\text{g/g}$), multiplied by riverine inputs of PSP and BEPS (in mg/l). Also added are the phytoplankton Se loads using a Se:C ratio and chlorophyll concentrations. The data sources used to define these inputs are shown in Figure 2-16. Box 5 explains the role of the Delta in particulate selenium transport.

Particulate selenium concentrations associated with PSP were previously reported by Doblin et al. (2006) and showed a range of values. Particulate selenium concentrations from riverine end members are $0.615 \pm 0.205 \mu\text{g/g}$ at the Sacramento River and $0.655 \pm 0.410 \mu\text{g/g}$ at the San Joaquin River (Doblin et al. 2006). Particulate elemental selenium ranged from $0.08\text{--}0.40 \mu\text{g/g}$ ($0.149 \pm 0.108 \mu\text{g/g}$), particulate selenite and selenate range from non-detectable to $0.25 \mu\text{g/g}$ ($0.270 \pm 0.137 \mu\text{g/g}$), and organic selenide concentrations ranged from $0.015\text{--}0.74 \mu\text{g/g}$ ($0.134 \pm 0.238 \mu\text{g/g}$) at Sacramento River at Rio Vista (Doblin et al. 2006). Particulate selenium measured at this location by Doblin et al. (2006) may possibly be influenced by the bay, particularly during low flow. During high flow, particulate selenium at this location may better reflect input from the Sacramento River. Concentrations associated with PSP at the head of the estuary (Rio Vista) are calibrated parameters. Once calibrated, selenium concentrations on particulates were kept constant through the simulation period of 1999-2006.

Particulate selenium loads from the San Joaquin River were estimated based on TSP loads and estimated particulate selenium concentrations from dissolved selenium concentrations (using species-specific K_d values derived based on data from the Delta, Appendix 4) for San Joaquin River at the confluence. If the San Joaquin River has higher particulate selenium concentrations, then mixing with Sacramento River and bay water may lower the concentrations. Data on particulate selenium further upstream would be needed to more directly estimate this particulate source, and no such data have been reported. However, from the standpoint of the model representation here, the San Joaquin River enters the bay through the Delta, and the effects of the Delta on the particulate selenium cannot be neglected. Particulate selenium concentrations have not been measured in San Joaquin River upstream from the Delta, yet, the river forms a conduit for transporting potentially large loads of particulate selenium from Central Valley to the Bay. The magnitude of the particulate load and the impact of the Delta on delivery of this load to the Bay need further studies/considerations.

Seawater endmember concentrations of PSP associated particulate selenium can be derived from model calibration, or observed concentrations at the Central Bay by Doblin et al. (2006) can be used. For the calibration presented here, a value of $1.22 \mu\text{g/g}$ was used as the seawater boundary condition, based on calibration. Because the seawater boundary condition is somewhat poorly defined, calculations were also presented with a range of boundary conditions from 0.96 to $1.22 \mu\text{g/g}$, as discussed in Section 4.

Selenium concentrations in bed sediment were derived from Meseck (2002) along the longitude of the estuary as shown in Table 2-11 (at distance = 0). Seawater endmember concentrations of BEPS-associated particulate selenium were specified as 0.

Particulate selenium associated with phytoplankton is assumed to have a riverine boundary concentration of 15.9 $\mu\text{g Se/g C}$ (Baines et al. 2004). The observed time-series data of chlorophyll a concentrations at Rio Vista and a C: Chl a ratio of 51 were used to estimate particulate selenium inputs associated with phytoplankton. The C:Chl a ratio of 51 was derived from Alpine and Cloern (1992) and used as the Delta input. This value was based on an average of the carbon:Chl a uptake ratio in the bay. C:Chl a ratios vary with phytoplankton species and growth phase, and a wide range of values has been reported in the literature (e.g., 10 to > 300, reviewed by Cloern et al., 1995; and 27-67 by Riemann et al., 1989). Variation of chlorophyll a content in phytoplankton in space and time was beyond the scope of this application and the Alpine and Cloern (1991) value was used throughout the calculation. The seawater end member of particulate selenium associated with phytoplankton is specified at 21.0 $\mu\text{g Se/g C}$. This number is in the range of the particulate selenium concentrations in phytoplankton found in the North San Francisco Bay, listed in Table 2-2.

Particulate selenium concentrations from different endmembers including the bed sediments, water column, riverine inputs from Sacramento at Rio Vista, San Joaquin River, Golden Gate, and phytoplankton are shown in Figure 2-23. The particulate selenium concentrations in the water column are closest to concentrations from Rio Vista and the Golden Gate, and were higher than concentrations in bed sediments. This suggests the influence from bed sediments on seston particulate selenium is not as significant as expected in other estuaries. Although the contribution may be small, the process of interaction with bed sediments is simulated by the model.

Table 2-10
Selenium Concentrations Associated with PSP Used in the Model for
Sacramento River at Rio Vista (after Meseck, 2002)

	Elemental Selenium in PSP ($\mu\text{g/g}$)	Selenate and Selenite in PSP ($\mu\text{g/g}$)	Org. Selenide in PSP ($\mu\text{g/g}$)
Mean	0.270	0.149	0.134
Standard Deviation	0.137	0.108	0.238
Range	N.D. to 0.25	0.08 – 0.4	0.015 – 0.74

Table 2-11
Selenium Concentrations Associated with BEPS used in the Model (after Meseck, 2002)

Distance from Sacramento at Rio Vista (km)	Elemental Selenium in BEPS ($\mu\text{g/g}$)	Selenate and Selenite in BEPS ($\mu\text{g/g}$)	Org. Selenide in BEPS ($\mu\text{g/g}$)
0.0	0.123	0.052	0.079
15.0	0.123	0.052	0.079
25.4	0.109	0.058	0.120
27.5	0.110	0.047	0.070
41.6	0.099	0.045	0.072
53.0	0.118	0.061	0.092
66.2	0.099	0.052	0.080

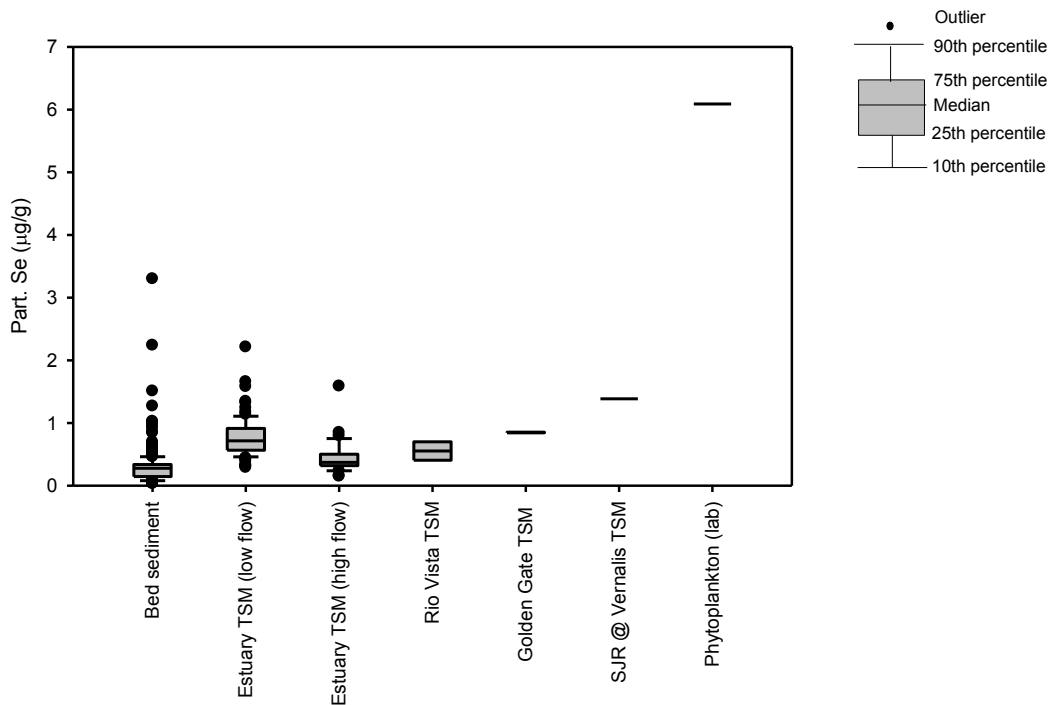
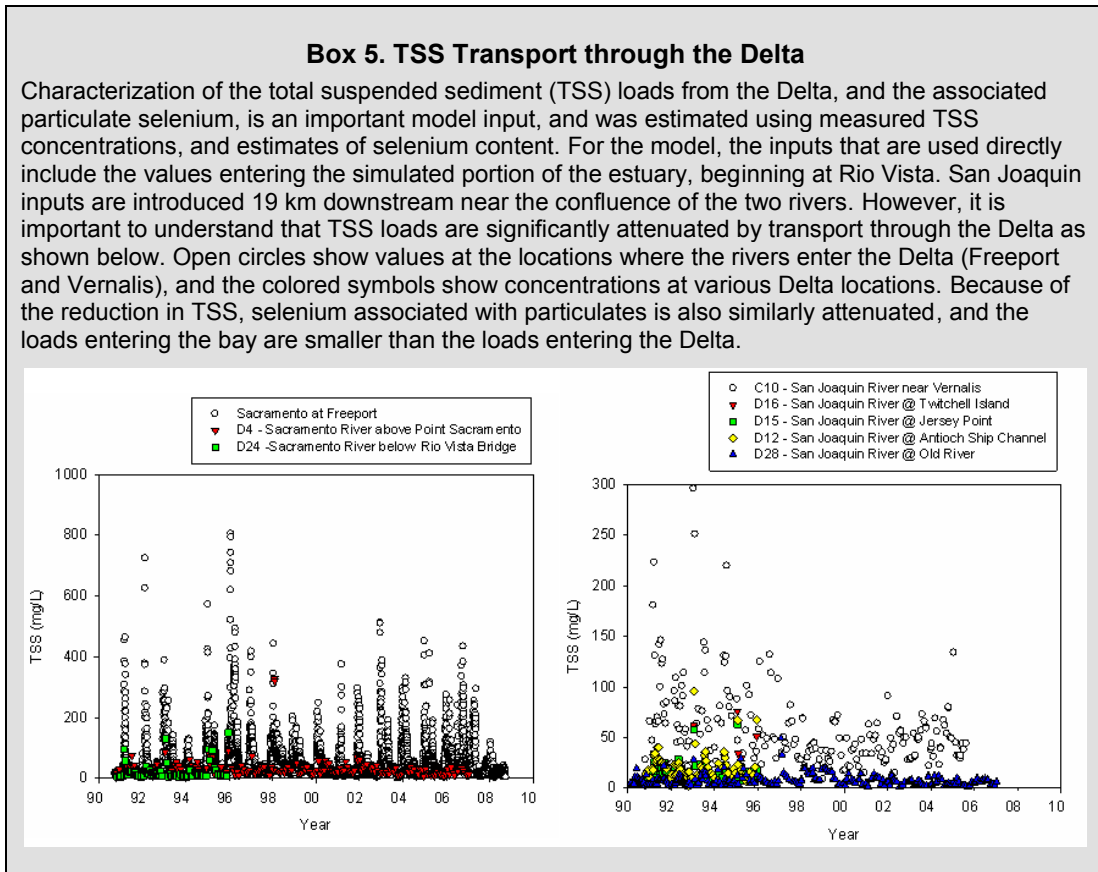


Figure 2-23 Observed particulate selenium concentrations from different endmembers (Source: RMP, Doblin et al. 2006).

Particulate selenium loads from the Delta were previously estimated using annual TSS loads from the Delta estimated by McKee et al. (2006) and selenium concentrations on particulates from Doblin et al. (2006) (Tetra Tech 2008a). McKee et al. (2006) estimated TSS loads from the Delta based on measurements at Mallard Island and accounted for both advective and dispersive fluxes. In this model application, as noted above, riverine inputs of particulate selenium are estimated as PSP and BEPS loads multiplied by selenium concentrations on particulates. The two methods yield similar annual particulate selenium loads to the Bay (Figure 2-19). Estimated particulate selenium loads from the Sacramento River at Rio Vista are greater than the San Joaquin River (Figure 2-24). Particulate selenium loads from the Sacramento River at Freeport and San Joaquin River are Vernalis are greater than the loads entering the Bay due to deposition in the Delta (Figure 2-25).

Particulate selenium loads from POTWs, refineries and tributaries are assumed to be zero.

South San Francisco Bay selenium loads into the Central Bay were also estimated for the model, although model testing showed that concentrations in NSFB were relatively insensitive to loads from the South Bay. The load was based primarily on contributions from the Guadalupe River because of high observed selenium concentrations. Flow from the Guadalupe River ranges from 35.63 Mm³/yr to 126.73 Mm³/yr. Average selenium concentrations in the Guadalupe River were 4.76 µg/L (Tetra Tech, 2008a). The estimated selenium loads that enter the South Bay range from 169.6-603.2 kg/yr. Speciation data are not available for the South Bay for recent years. The loads were assumed to be in dominantly in the selenate form and not retained significantly in South Bay. Given the insensitivity of the NSFB concentrations to South Bay loads, the load was not varied from year to year, and a median value 365 kg/yr of selenium load (as selenate) from South Bay was used for all years of the simulation. No particulate selenium contribution from the South Bay was assumed.

2.10. SUMMARY OF MODELING APPROACH

Although complex, the approach presented here makes the best available use of existing information in NSFB that influences selenium loads, transformations and biological uptake. To the extent feasible the inputs are derived for a time frame spanning 1999-2006. Over this time, relatively complete data records were available for flows, chlorophyll a, suspended sediments, and salinity.

For total selenium, all known inputs relating to riverine sources, point sources, and local tributaries have been represented in this work. There were generally good data records for most point sources, including refineries, POTWs, and the San Joaquin River. Not all total selenium data were fully defined over the entire period 1999-2006, and two approaches were used to fill in the gaps. For riverine loads for the Sacramento and San Joaquin Rivers and for the local tributaries to the bay, relationships were developed between flows and concentrations, and these relationships were used to estimate concentrations, and thus loads, for dates during which selenium measurements were not available. For point sources, where daily data were not available for the entire period, primarily POTWs and non-refinery industrial discharges, an average daily load was computed, and was applied over the entire period of the simulation.

In contrast to total selenium data, speciation information relating to the sources was only available for a limited number of dates ending in 1999. Speciation of source loads for other years was largely based on data from 1999.

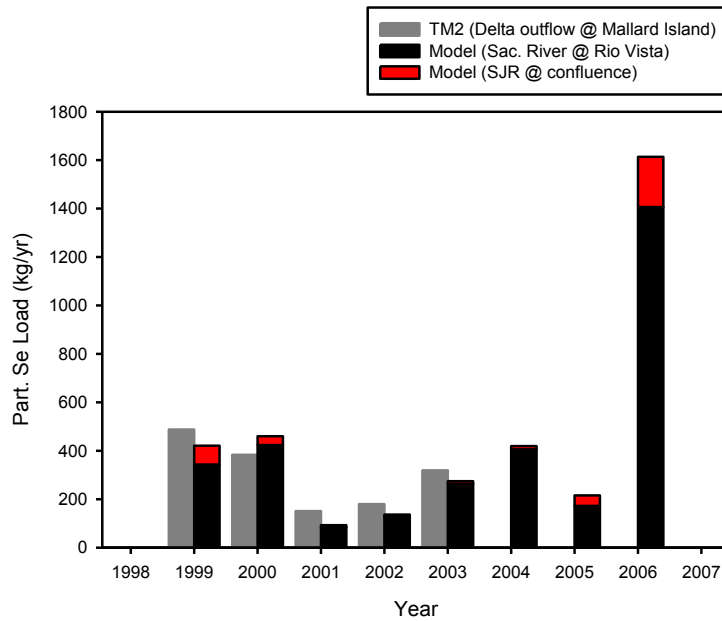


Figure 2-24 Particulate selenium inputs to the Bay estimated in TM2 (Tetra Tech, 2008a) and in the model. The TM-2 load estimates were computed using measured suspended sediment outflow from the Delta, multiplied by the average selenium content on particles ($0.64 \mu\text{g/g}$). The approach used for the model was based on riverine flows, flow-TSS relationships, and partitioning between dissolved and particulate phases. For years during which both methods apply (1999-2003), the load estimates are similar.

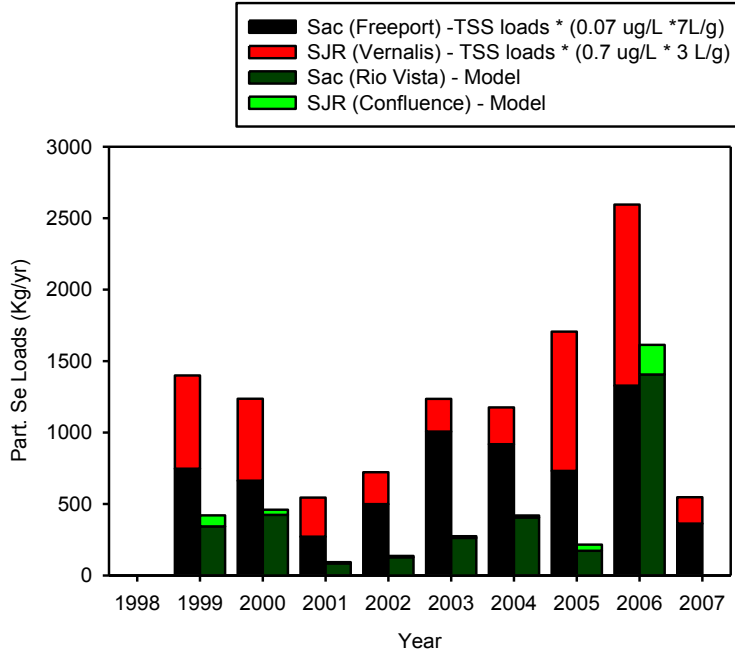


Figure 2-25 Loads estimated upriver at Freeport (Sacramento River) and Vernalis (San Joaquin River) compared to model inputs of particulate selenium loads to the bay from the two rivers at Rio Vista (Sacramento River) and a point on the San Joaquin River near the confluence with the Sacramento River. Dissolved selenium concentrations and partitioning coefficients for Sacramento River at Freeport and San Joaquin River at Vernalis were data from Cutter and Cutter (2004) and Doblin et al. (2006) for 1998-2000. The estimates show a significant reduction of particulate selenium from the two rivers during transport through the Delta (also see Box 4).

3. MODEL CALIBRATION AND EVALUATION

3.1. CALIBRATION PROCESS

The model calibration involved the selection of a variety of parameters to represent processed in NSFB. Some model parameters and inputs are poorly quantified given the available dataset or show a wide range, and calibration is needed to obtain the best fit of the model prediction to the observed values, whereas others are relatively well-quantified in the literature or available data. The latter include the bathymetry and total length of the estuary, parameters used to simulate tidal variation, flow from the rivers, and point-source loads. Meseck (2002) classified model parameters into three categories: well-known parameters, moderately known, and poorly known parameters (Table 3-1). Parameters obtained directly from the literature without fitting are listed in Table 3-2.

Because the model as generally formulated in Section 2, has previously been calibrated, (Meseck, 2002; and Meseck and Cutter, 2006), minimal changes were made to previously calibrated parameters. The parameters adjusted are constrained by values reported in the literature. Parameter values that were derived through calibration were generally moderately or poorly known parameters, as listed in Table 3-3.

Table 3-1
Classification of Parameters Needed in ECoS to Simulate the
Biogeochemical Cycle of Selenium in NSFB (after Meseck, 2002)

Well-known Parameters	In Equation
River flow	(30)
Cross section area	
Refinery inputs	
Tidal amplitudes	(8)
Irradiance	
Initial salinity	
TSM	
Moderately-known Parameters	
P_m – maximum photosynthesis rate	(10)
α - slope of light saturation curve	(10)
r-respiration rate	(9)
W- zooplankton weight	(A1)
k_1 - k_3 – dissolved selenium oxidation rate constants	(14-16)
Z – zooplankton abundance	
Selenium concentration in bottom sediment	(A2)
Poorly-known Parameters	
d, e, ϵ and ψ - scaling factors to simulate transport of bed exchanged particulate material	(4) (5)
k_s – light attenuation coefficient	
k_4 - k_6 – phytoplankton uptake rates of selenite, selenate, and organic selenide	(13)
Delta removal constant of selenium	(14-16)
Tributary loads	

Table 3-2
Parameter Values Derived from the Literature (after Meseck, 2002)

Parameter	Description	Value	Units	Reference
M ₂ phase	Tidal phase	125	degrees	Godin (1972)
K ₁ phase	Tidal phase	264	degrees	Godin (1972)
O ₁ phase	Tidal phase	51	degrees	Godin (1972)
M ₂ frequency	Tidal frequency	595.52	Degrees/d	Godin (1972)
K ₁ frequency	Tidal frequency	360.96	Degrees/d	Godin (1972)
O ₁ frequency	Tidal frequency	334.56	Degrees/d	Godin (1972)
M ₂	Tidal amplitude	0.58	m	Uncles and Peterson (1996)
K ₁	Tidal amplitude	0.37	m	Uncles and Peterson (1996)
O ₁	Tidal amplitude	0.23	m	Uncles and Peterson (1996)
V _s	Sinking rate of BEPS	86.4	m/d	McDonald and Cheng (1997)
BEPS _{sea}	Sea water end member of BEPS	0	g/d	Harris et al. (1984)
PSP _{sea}	Sea water end member of PSP	0.01	g/L	Harris et al. (1984)
ws	Sinking rate of phytoplankton	0.5	d ⁻¹	Lucas et al. (1998)
W	Zooplankton weight	13	mg C/animal	Hutchinson (1981)
B _{sea}	Initial phytoplankton concentrations and seawater end member	2.3	µg Chl-a/l	Alpine and Cloern (1992)
r _{phyto}	Non-specific mortality	0.1	d ⁻¹	Cole and Cloern (1994)
C:Chl a	Carbon to Chl a ratio	51	mg C/mg Chl a	Alpine and Cloern (1992)
k ₃	Rate constant, SeIV-> SeVI	2.4 × 10 ⁻⁶	d ⁻¹	Cutter and Bruland (1984)
k ₄	Uptake rate of SeIV by phytoplankton	15.78 0.00076	1/(g Chl a)/hr l/day (under chl a = 2 µg/L)	Riedel et al. (1996)
k ₅	Uptake rate of SeVI by phytoplankton	3.37 0.00016	1/(g Chl a)/hr l/day (under chl a = 2 µg/L)	Riedel et al. (1996)
k ₆	Uptake rate of Org Se-II by phytoplankton	7.89 0.00038	1/(g Chl a)/hr l/day (under chl a = 2 µg/L)	Riedel et al. (1996)
Z	Zooplankton abundance	30-230	Animal/L	Pukerson et al. (2003)
Phyto Se:C river	Phytoplankton Se in the river	15.9	Ratio	Baines et al. (2004)
Phyto Se:C sea	Phytoplankton Se in seawater	23.9	Ratio	Doblin et al. (2006)

**Table 3-3
Parameter Values Derived Through Model Calibration**

Parameter	Description	Value	Standard Deviation	95% Confidence Interval	Units	Literature Range	Reference
kw	Dispersion coefficient	362	± 16	362 ± 7.7	m/s ²	16-812	Cifuentes (1990)
a	Resuspended sediment at river end member	0.0046			g/L		Calibration
b	Permanently suspended sediment at the riverine end	0.00029			g/L		Calibration
c	Scales freshwater discharge to sediment input	0.7					Calibration
d	Scaling factor for Ubeps	0.322					Calibration
e	Scaling factor for Ubeps	793					Calibration
ε	Scaling factor for Kbeps	1.99			m		Calibration
ψ	Scaling factor for Kbeps	3.2e6			m		Calibration
P _m	Maximum rate of photosynthesis	100.6	± 1.50	100.6 ± 0.72	mg C/mg Chl-a/d	24-219	Alpine and Cloern (1992)
α	Slope of light-saturation curve divided by P _m	0.00397			Einst.m ² /d	0.002-0.009	Peterson and Festa (1984)
P _b	Benthic grazing rate	0.037	± 0.002	0.037 ± 0.001	d ⁻¹		
k ₁	Rate constant, pSe-II -> d org Se-II	0.0066			d ⁻¹	1.3 x 10 ⁻⁵ - 5 x 10 ⁻²	Cutter (1992)
k ₂	Rate constant, d org Se-II -> SeIV	0.004			d ⁻¹	1.0x10 ⁻³ – 81.0	Cutter (1992)
Se OPSP	Elemental selenium in PSP at Rio Vista	0.100	± 0.034	0.100 ± 0.016	µg/g	0.08-0.40	Calibration; Doblin et al. (2006)
Se (IV+VI)PSP	Se IV+VI selenium in PSP at Rio Vista	0.202	± 0.016	0.202 ± 0.008	µg/g	0-0.25	Calibration; Doblin et al. (2006)
Org. Se-II PSP	Org. Se-II selenium in PSP at Rio Vista	0.166	± 0.076	0.166 ± 0.076	µg/g	0.015-0.74	Calibration; Doblin et al. (2006)
Delta –San Joaquin River input constant (1- removal constant); dissolved species only	fSeVI	0.260	± 0.125	0.260 ± 0.060			Calibration
	fSeIV	0.326	± 0.232	0.326 ± 0.112			Calibration
	fSeII	0.534	± 0.342	0.534 ± 0.165			Calibration
a'	adsorption	0.0013			l/g/d	0.1-0.8	Zhang and Sparks (1990)
BEPSriver	Riverine end member of BEPS	0.00463			g/L		Harris et al. (1984)

Calibration of the model followed the sequence of fitting physical variables (salinity and TSM), followed by biological (e.g., phytoplankton) and chemical variables (dissolved and particulate selenium). The sequence selected is such that parameters calibrated in subsequent steps do not affect prior parameters. Thus, calibration of parameters related to phytoplankton will not change the parameters fitted for salinity. Likewise, parameters for selenium species will not have an effect on the salinity, phytoplankton, or TSM. The fitting process was as follows:

Step 1: Salinity (1 parameter)

Step 2: TSM (4 parameters)

Step 3: Phytoplankton (3 parameters)

Step 4: Dissolved selenium species (selenate, selenite, and selenide) (5 parameters, and the delta removal constants for each species)

Step 5: Particulate selenium (elemental selenium, selenite+selenate, selenide) (3 parameters)

The dataset used in calibrating the physical variables (salinity, TSM) and phytoplankton were obtained from the USGS (<http://sfbay.wr.usgs.gov/access/wqdata/>). The main calibration time periods for these parameters are roughly on monthly intervals from January 1999 to December 1999. Data used in calibration include 19 USGS monitoring stations located in the North Bay as shown in Figure 1-4. As discussed below, data for these constituents were measured at a higher frequency than the selenium data (typically every two months).

The model calibration for selenium was mainly performed using data from 1999. Water year 1999 has detailed selenium speciation data sampled during low and high flow periods. Water year 1999 also represents conditions for which detailed refinery discharge data are available. Further, refinery loads were decreased by about two-thirds in mid-1998, and have stayed at approximately those levels since that time. Thus, 1999 data represent post refinery-cleanup conditions, and are somewhat representative of more recent conditions. Importantly, no detailed speciation data on selenium are available after 1999.

For the application in the NSFB, the model was run on a time step of 1 day. The spin-up time for model simulation is approximately 180 days starting from June 1, 1998.

The model calibration was conducted based on a least squares minimization approach, using a fitting program provided by Dr. John Harris, the developer of the ECoS code (Harris, 2003). For each iteration, the sum of square deviation between observed and simulated values was calculated by the program and the parameters were adjusted for the next iteration to minimize the sum of square errors. Estimates of mean and standard deviation of the parameters calibrated and sum of squared deviation are provided by the program as calibration results. Example results are shown in Appendix 3.

The DYMBAM component of the model does not require model fitting, and was applied after the other physical, biological, and chemical variables were computed.

The model goodness of fit was evaluated using two measures: the correlation coefficient (r) between predicted and observed values, a goodness of fit defined in Perrin et al. (2001).

$$GOF(\%) = 100 * \left(1 - \left| \frac{\sum X_{cal}}{\sum X_{obs}} - \frac{\sum X_{obs}}{\sum X_{cal}} \right| \right) \quad (29)$$

where, X_{cal} is the model simulated concentration and X_{obs} is the observed concentration. A 100% goodness of fit indicates a perfect fit between simulated and observed values.

The dates selected for calibration of selenium speciation and transformation are April 13, 1999 (high flow) and November 11, 1999 (low flow), with available data from Cutter and Cutter (2004) and Doblin et al. (2006). Because selenium data were collected based on salinity intervals, locations of sample stations vary during low and high flow. For model calibration, station pairs for April and November that are in close proximity were lumped as one station and resulted in a total of 13 stations with two data points in time. The data pairs with dissolved selenium concentrations are shown in Figure 3-1. As shown in Figure 3-1, selenate concentrations were elevated in the middle of the estuary during low flow, corresponding to relatively higher point source inputs. For selenium, the calibration follows the sequence of selenate, organic selenide and selenite, particulate elemental selenium, particulate organic selenide and particulate adsorbed selenite. Organic selenide can be oxidized to selenite, therefore it can influence selenite and was calibrated first. Particulate selenium is influenced by dissolved selenium through phytoplankton uptake and adsorption and therefore was calibrated after dissolved selenium.

Although the sequence of parameter fitting employed here was selected such that parameters related to one constituent did not affect previously fitted parameters, multiple parameters/processes can affect one common constituent and there is no clear guidance on selecting a parameter to fit first. In principle, when there are multiple parameters in a single differential equation representing a constituent, it may be better to calibrate using multiple parameters simultaneously; however, calibrating multiple parameters at the same time sometimes resulted in negative or unrealistic values and resulted in significantly longer run times. Therefore, the final set of parameters presented here were based on calibration of one parameter at a time, performed in five sequential steps for each major class of constituent.

The following sections describe the calibration process of each parameter in the model.

3.1.1 Salinity

In ECoS, salinity is mostly determined by boundary conditions and hydrological forcings that affect mixing (river flow, tides). Inputs for simulating salinity are generally well quantified. The salinity is simulated as a result of advection and dispersion. Dispersion is simulated using a single dispersion coefficient (K_w), which reflects the result of mixing. Calibration for salinity mainly involves adjusting the dispersion coefficient K_w . In Meseck (2002), salinity was modeled as a dynamic function of salinity gradient and velocity, which may result in linear salinity profiles. K_w calibrated based on monthly observed salinity data in 1999 indicates dispersion coefficient varies across the year, but generally ranges between 254 – 538 m^2/s . However no relationship between K_w and flow was found. Therefore, for 1999, the estimated monthly K_w values were used in the model simulation. K_w values between sampling dates were linearly interpolated by the model. For time periods after 1999, K_w used is the calibrated value (362 m^2/s) based on all data in 1999. The calibrated K_w value using all data in 1999 results in relatively low standard deviation (Table 3-3).

3.1.2 TSM

Calibration for TSM involved adjusting parameters that determine location and shape of estuarine turbidity maximum (d, e, ϵ and ψ) and riverine boundary conditions that define concentrations at the head of the estuary. Riverine concentrations of TSM simulated using equation (27) compared well with observed TSM at Sacramento River at Rio Vista (12-42 mg/L observed vs. 20-45.6 mg/L simulated at the head of boundary).

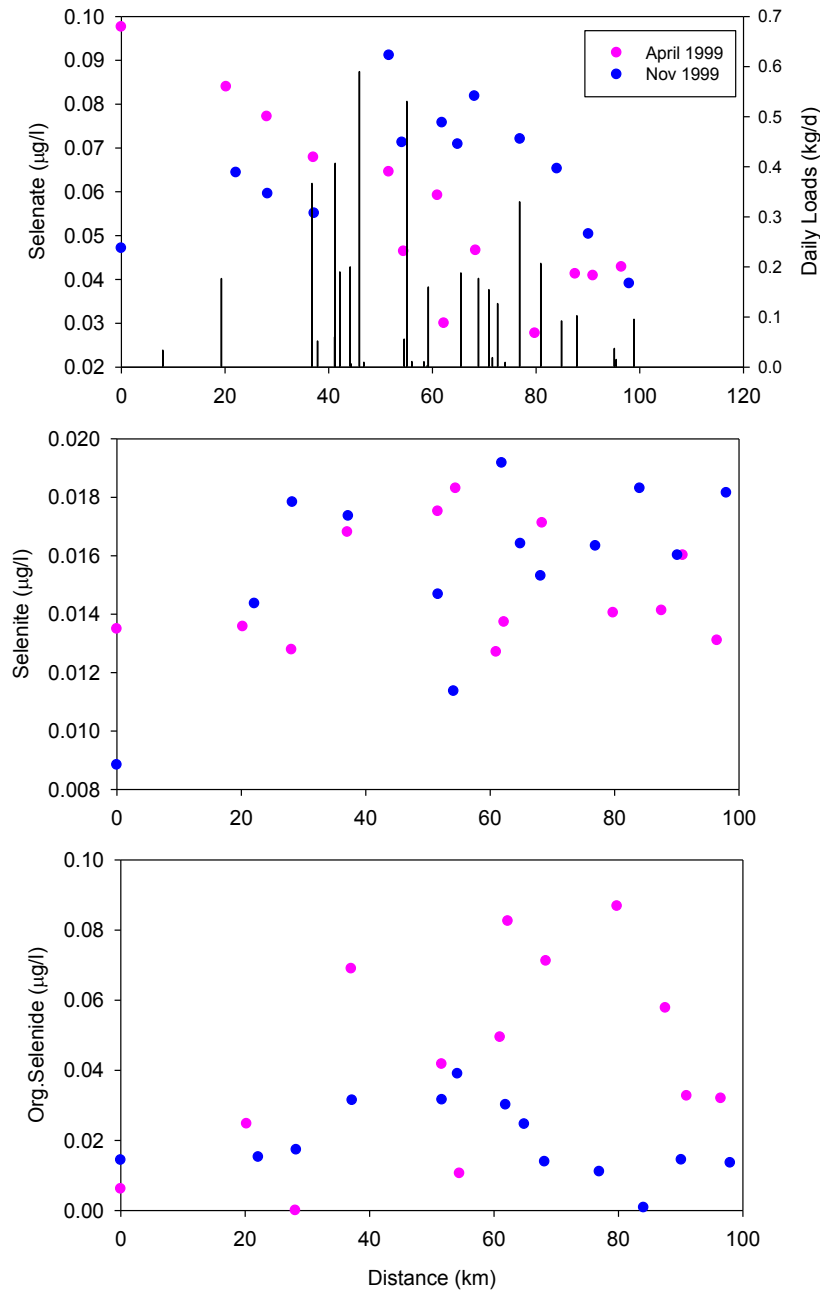


Figure 3-1 Dissolved selenium concentrations for stations used in calibration, with mean daily loads from refineries, tributaries, and POTWs shown. Data points shown are individual values.

3.1.3 *Phytoplankton*

Calibration of phytoplankton involved adjusting parameters related to zooplankton grazing. Spatial distribution of zooplankton abundance was derived from Pukerson et al. (2003). Grazing was assumed to occur during summer months between June-October, and was held at zero for most months for the rest of the year. The calibration involves varying the grazing rates across the grazing months. The other parameter calibrated is the maximum rate of photosynthesis (*Pm*). Estimated standard deviation for the calibrated *Pm* is small (Table 3-3).

3.1.4 *Dissolved selenium*

Concentrations of different species of dissolved selenium from riverine inputs are simulated using the same sine wave function as in Meseck (2002), with parameters listed in Table 2-8. A key parameter with significant uncertainty is the Delta load removal constant, which is adjusted to predict dissolved selenium concentrations. The calibrated San Joaquin River load constants (1 – removal constant; for convenience) range between 0.268 (selenate) – 0.558 (organic selenide) for different species. The calibrated load constants have relatively large standard deviation or coefficient of variance. The coefficients of variation are about 50% (0.446 – 0.557), suggesting the relatively large uncertainties in the San Joaquin River loads.

Selenite uptake rates by phytoplankton measured by Baines et al. (2004) at ambient selenite concentrations (0.29 nmol/l) similar to the observed selenite concentrations in the NSFB were first used. Uptake rates measured by Baines et al. (2004) in laboratory tests were 0.33 pmol Se/($\mu\text{g Chl a}$)/hr. However, the uptake rates result in Se:C ratios much higher than observed values of 15.9 $\mu\text{g/g}$ in the Delta. Therefore, lower uptake rates (normalized to ambient selenite concentrations), as in Riedel et al. (1996) and in Meseck and Cutter (2006) were used, and a more reasonable selenium content (measured as Se:C ratio) in phytoplankton is predicted. Uptake rates of selenate and organic selenide were at 25% and 50% of selenite, as suggested in previous experimental studies (Riedel et al., 1996; Baines et al., 2001). Increasing organic selenite uptake rate to same as selenite did not result in significant changes in particulate organic selenide. This may be due to both low organic selenide concentration in the estuary and, even with the increase, relatively low uptake.

3.1.5 *Particulate selenium*

For particulate selenium, the key parameters for calibration are selenium concentrations in riverine inputs, which showed a range from 0.35 – 0.75 $\mu\text{g/g}$ (Doblin et al. 2006). The derived selenium concentrations in PSP are slightly higher than values used in Meseck (2002) at 0.05-0.10 $\mu\text{g/g}$ for each species.

The total riverine particulate selenium input for the year 1999 based on high flow particulate selenium concentration is 465 kg/yr. Calibrated selenium content on particulates by species at the head of the estuary generally shows relatively low standard deviation (Table 3-3). The total particulate selenium at Rio Vista is 0.46 $\mu\text{g/g}$ (sum of organic, inorganic, and elemental selenium). Higher selenium content on particulates may be expected during low flow (e.g., 0.75 $\mu\text{g/g}$ in Nov. 1999). Therefore the model was also run using a higher riverine particulate selenium concentration of 0.75 $\mu\text{g/g}$ for low flow period (river flow $< 1.5 \times 10^{10}$ l/d).

3.2. CALIBRATION RESULTS

Calibrated salinity profiles for months between January 1999 - November 1999 compare well to the monthly cruise data obtained from the USGS ($r > 0.95$; GOF = 85.0 - 99.8 %; Figure 3-2). The model is able to simulate salinity profiles along the longitude of the estuary under different flow conditions, for both high and low flow time periods (e.g. April 1999 and November 1999). Lower salinity was simulated during high flow and salinity increases as flow decreases. The high correlation between the observed and predicted salinity for all data points in 1999 indicates the model is able to simulate the salinity relatively well (Figure 3-3, $R^2 = 0.971$) without systematic error. The residuals plots indicate larger deviation (observed – predicted salinity) occur near the Central Bay (Figure 3-4). The deviation is also larger for the months of April and June (Figure 3-5). These two months correspond to the falling limb of the hydrograph when flow is changing rapidly. It may be due to the rapid change of flow that the value of the dispersion coefficient also changes.

Calibration for TSM shows less agreement with the observed data than salinity, especially peak concentrations. The model is able to capture the locations of ETM for several months, although it under-predicted the peaks of ETM (Figure 3-6). Simulated TSM for low flow periods compared moderately well with the observed values ($r = 0.28 - 0.92$; GOF = 55.1 – 99.6 %). The model under-predicted a few TSM peaks because fitting using the same set of parameters for both high and low flow is difficult. If ETM is captured well during high flow, the TSM may be over-predicted during low flow. Correlation between predicted and observed TSM for all data points in 1999 is reasonable given the complexity of the underlying processes (Figure 3-7, $R^2 = 0.536$). The data points evenly scatter around the 1:1 line (Figure 3-7), except when observed concentrations are greater than about 50 mg/l.

Fitting of phytoplankton data in the NSFB is difficult due to multiple factors affecting the phytoplankton dynamics. Also, using one general function for growth and grazing may not capture the local variability over extended periods of time. As with TSM, the model was better able to capture average concentrations than the spatial and temporal locations of peak values. The model under-predicted the observed increases in phytoplankton concentrations in the Central Bay for several months (September and October 1999; Figure 3-8). Phytoplankton concentrations at the head of the estuary seem to have a large impact on the simulated phytoplankton concentrations in the bay. Generally, the fit for phytoplankton is reasonable for most of the months ($r = 0.04 - 0.80$; GOF= 42.5 – 94.3%). For several months (e.g. June 1999), high chlorophyll a concentrations were observed in the upper estuary. These high concentrations are likely due to lower zooplankton abundance in the upper estuary during spring months. The data points of predicted and observed chlorophyll a concentrations for 1999 scatter around the 1:1 line, with some under-prediction at high numbers and some over-prediction ($R^2 = 0.36$). The under-prediction is most notable near the Central Bay. The high chlorophyll a concentration near Central Bay could be a result of advection from South Bay or changes in phytoplankton species in the Central Bay.

Simulated dissolved selenium concentrations during high flow for April 1999 indicated relatively conservative behavior of mixing along the estuary and compared relatively well with the observed data (Figure 3-10). The fit for selenate and selenite is reasonable as indicated by relatively high goodness of fit (GOF = 82.1% and 70.6%). Observed organic selenide shows large variations along the estuary. Organic selenide was measured as the

difference between total dissolved selenium and other species of dissolved selenium, therefore the data inherently represent larger uncertainties. Because total selenium was measured separately, these concentrations were reported more accurately.

Simulated dissolved selenium concentrations during low flow for November 1999 show good agreement with the observed data (Figure 3-10). The model is able to capture the elevated selenium concentrations during low flow. A mid-estuarine peak is evident given the local sources from tributaries and refineries, despite refinery load reductions in mid-1998. The model does well in capturing mid-estuarine peak concentrations in selenite, selenate, and organic selenide (Figure 3-11).

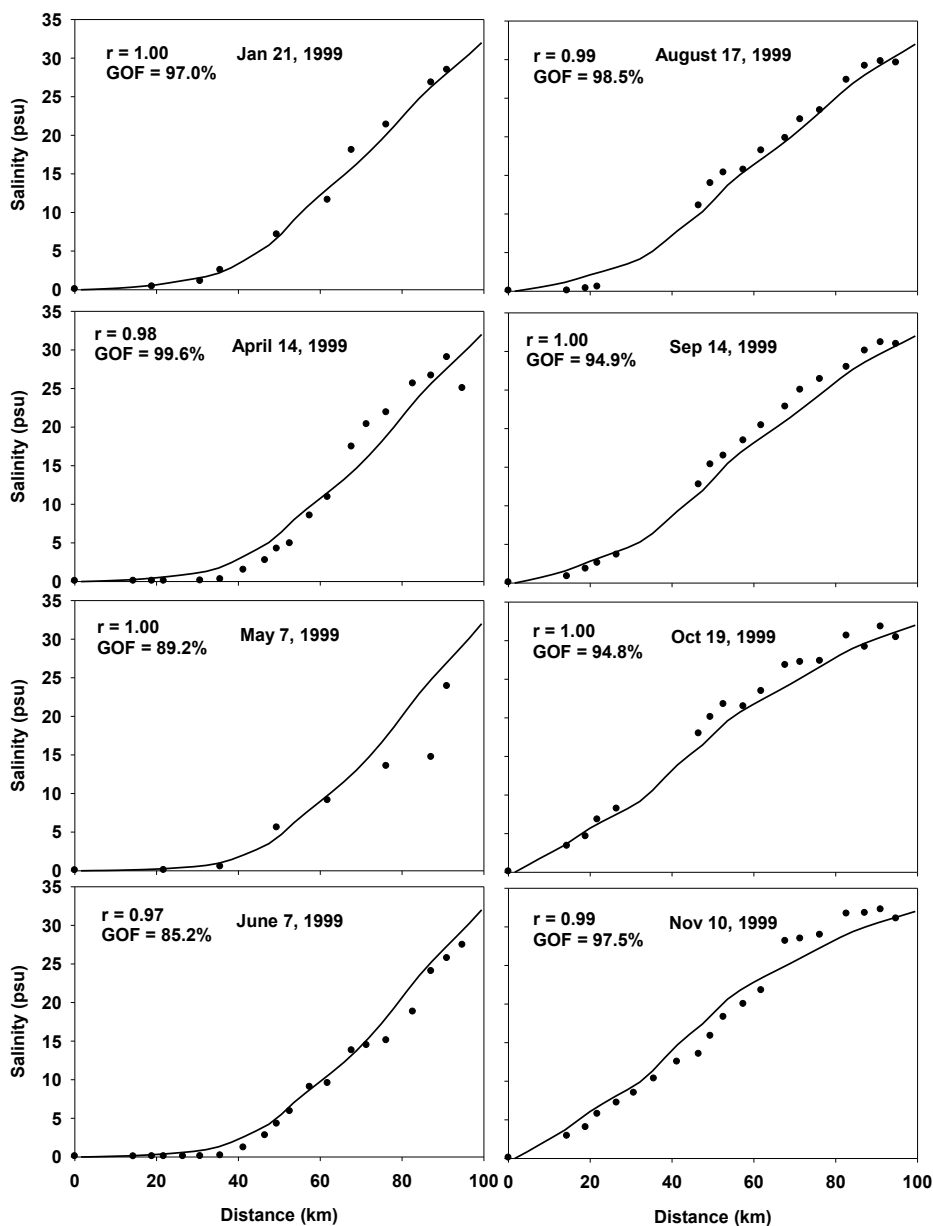


Figure 3-2 Simulated monthly salinity profiles compared to the observed data from the USGS

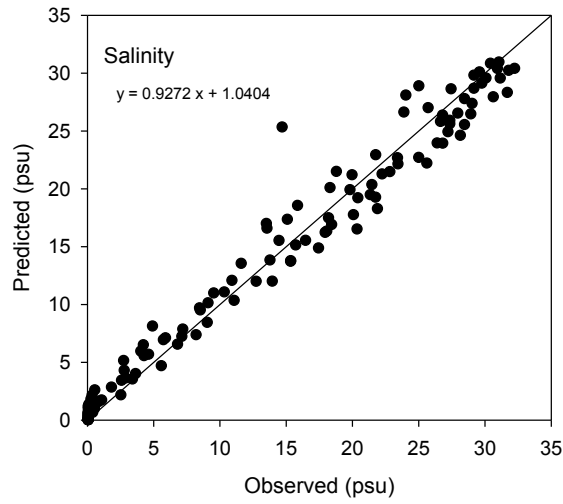


Figure 3-3 Comparison of predicted and observed salinity for different months for the calibration period of 1999.

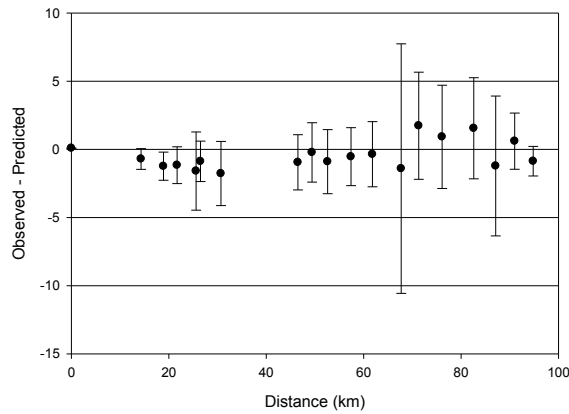


Figure 3-4 Deviation of observed and predicted salinity for 1999 across the estuary longitude profile

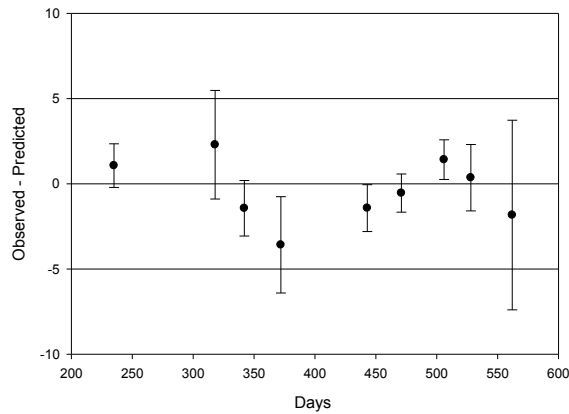


Figure 3-5 Deviation of observed and predicted salinity for sampling stations as a function of days from June 1st, 1998.

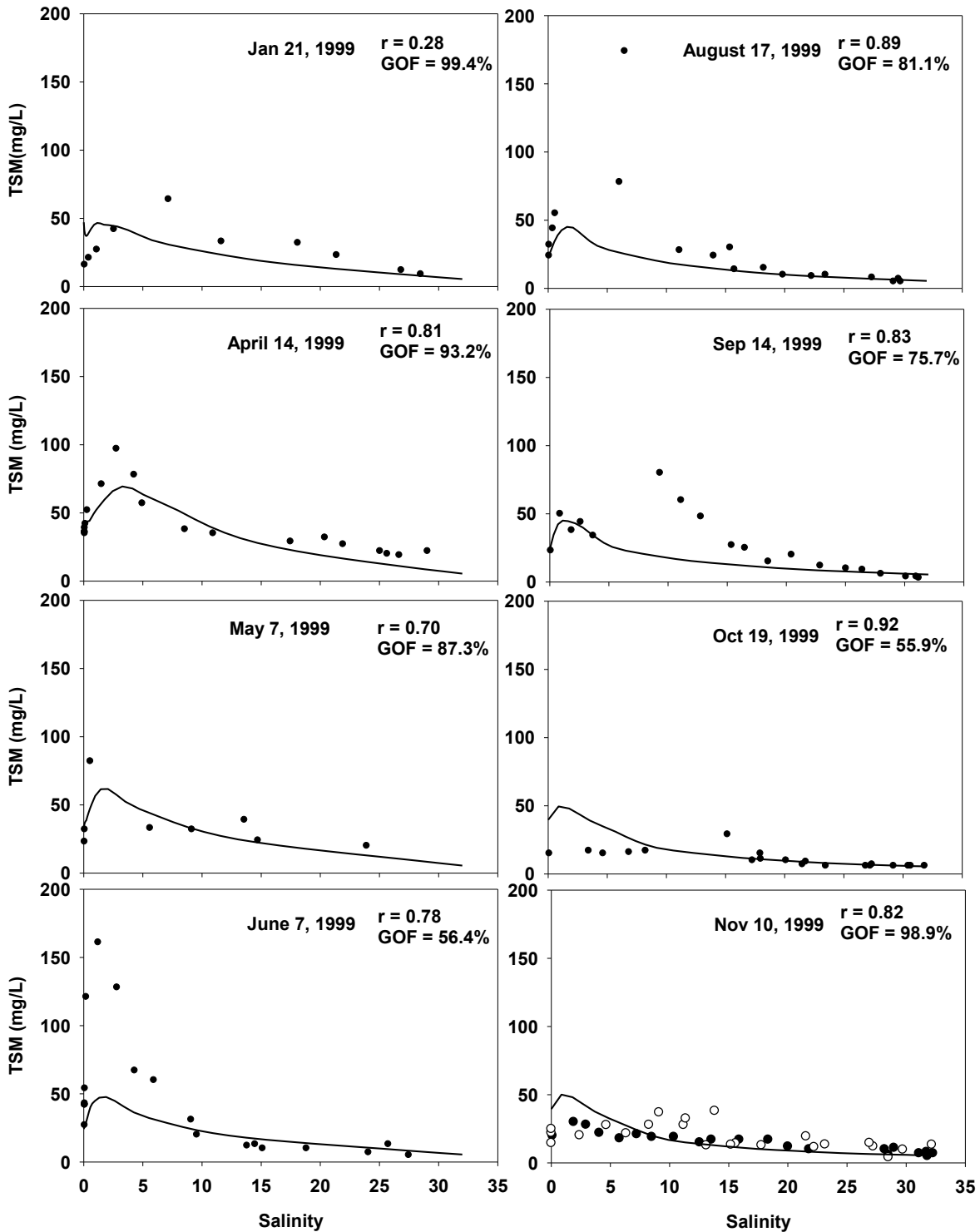


Figure 3-6 Simulated TSM concentration profiles along the salinity compared to the observed data from the USGS. Data collected by Cutter and Cutter (2004) are shown with open circles.

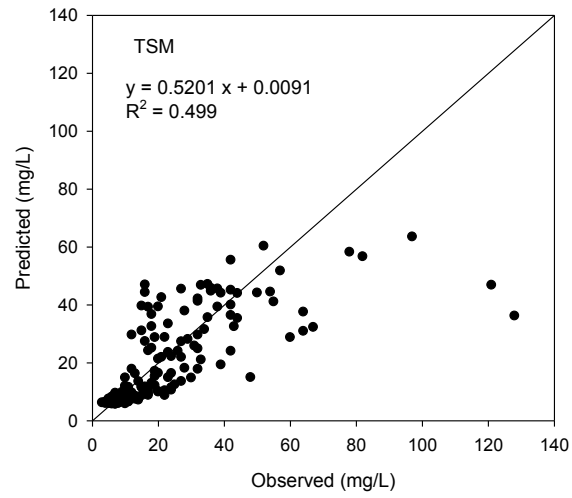


Figure 3-7 Comparison of observed and predicted TSM concentrations for different months in 1999.

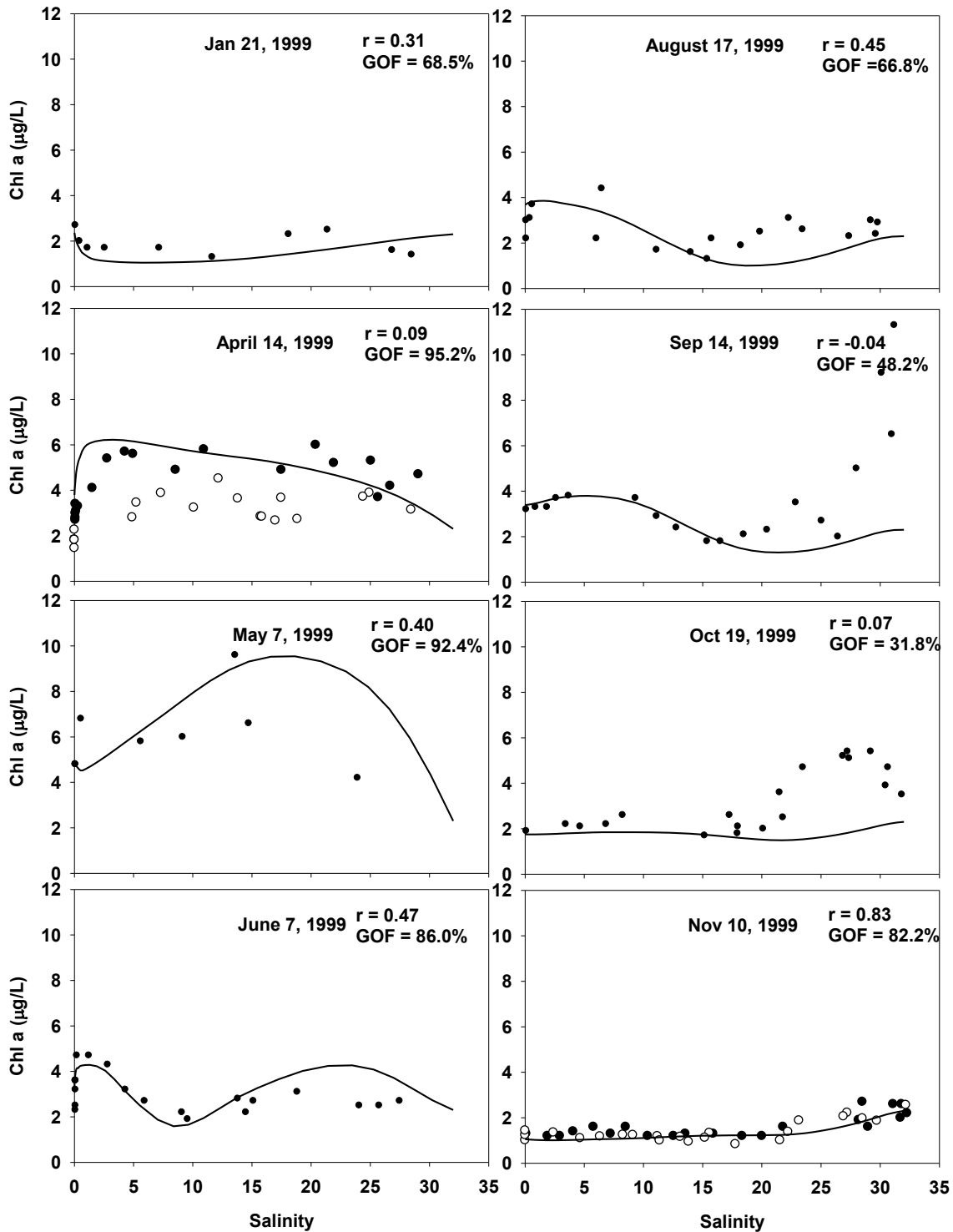


Figure 3-8 Simulated phytoplankton profiles compared to the observed data from the USGS. Chlorophyll a concentrations sampled by Cutter and Cutter (2004) are shown with open circles.

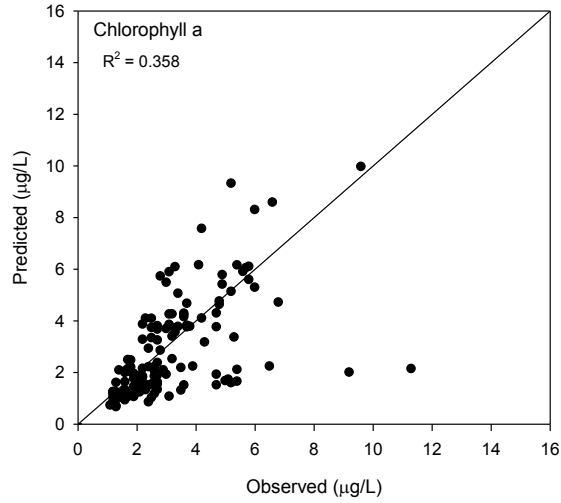


Figure 3-9 Comparison of observed and predicted chlorophyll a concentrations for different months in 1999.

Table 3-4 Evaluation of Goodness of fit for Model Calibration of Selenium for April and November 1999

		Selenate	Selenite	Org. Se	Particulate Selenite +Selenate	Particulate Elemental	Particulate Organic
April 13, 1999	r	0.400	0.067	-0.112	0.592	0.206	0.181
	GOF	78.4%	97.6%	46.3%	68.3%	83.2%	83.7%
November 11, 1999	r	0.539	0.314	0.568	0.487	0.208	0.087
	GOF	94.6%	97.5%	61.2%	90.2%	38.2%	94.7%

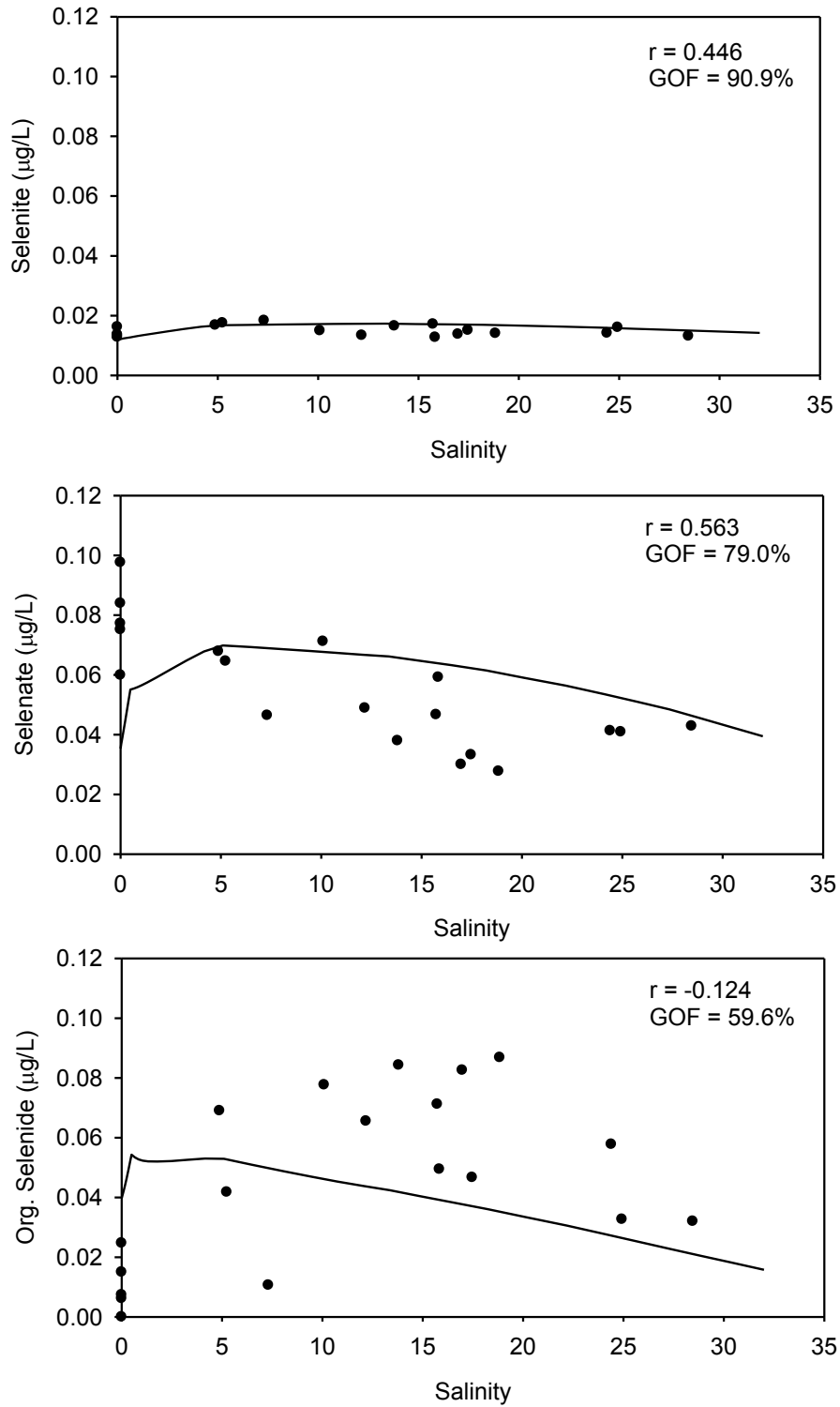


Figure 3-10 Model simulated dissolved selenium concentrations in different species compared to the observed data for April 1999.

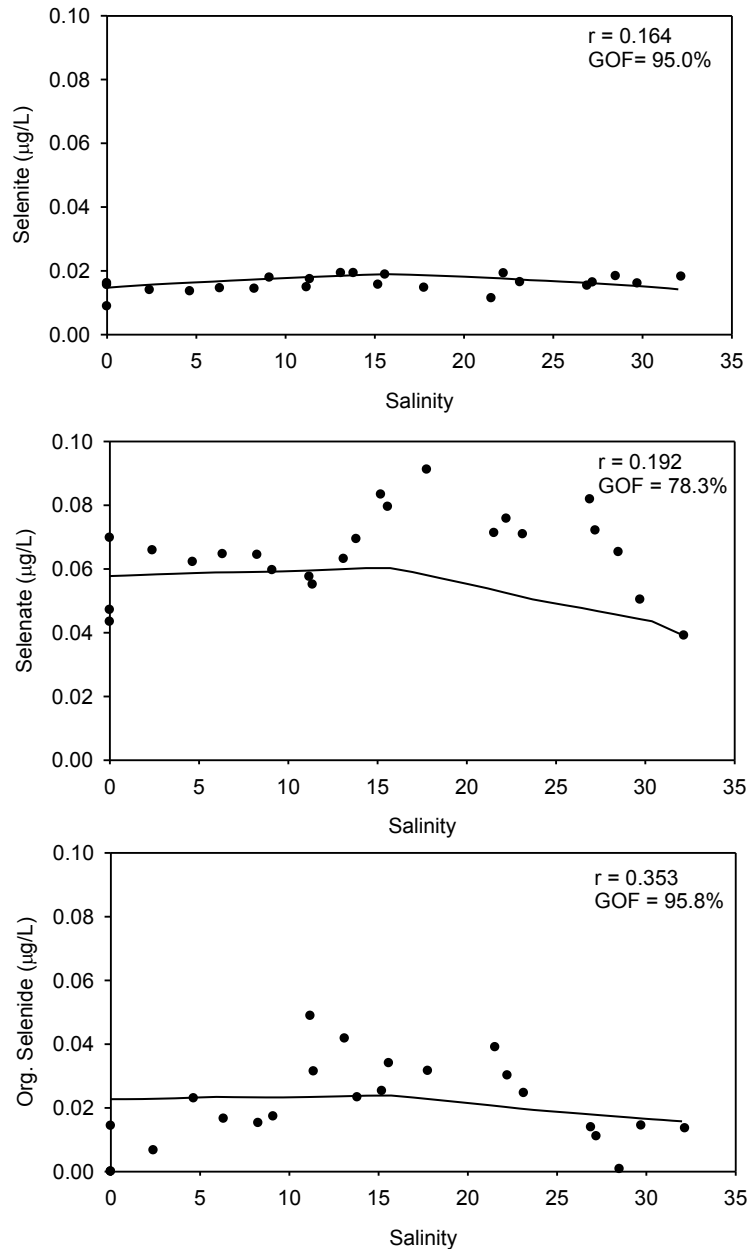


Figure 3-11 Model simulated dissolved selenium concentrations in different species compared to the observed data for November 1999.

Simulated particulate selenium concentrations (adsorbed selenite and selenate, elemental, and particulate organic selenide) show relatively conservative mixing behavior, decreasing with salinity and agree well with the observed data (Figure 3-12). Simulated particulate selenium concentrations for November 1999 along the salinity gradient generally agree with the observed data (Figure 3-13). Correlations between predicted and observed selenium concentrations are generally weak. However, predicted mean concentrations of different species of selenium (over different stations) compared well with the observed mean values (Table 3-5).

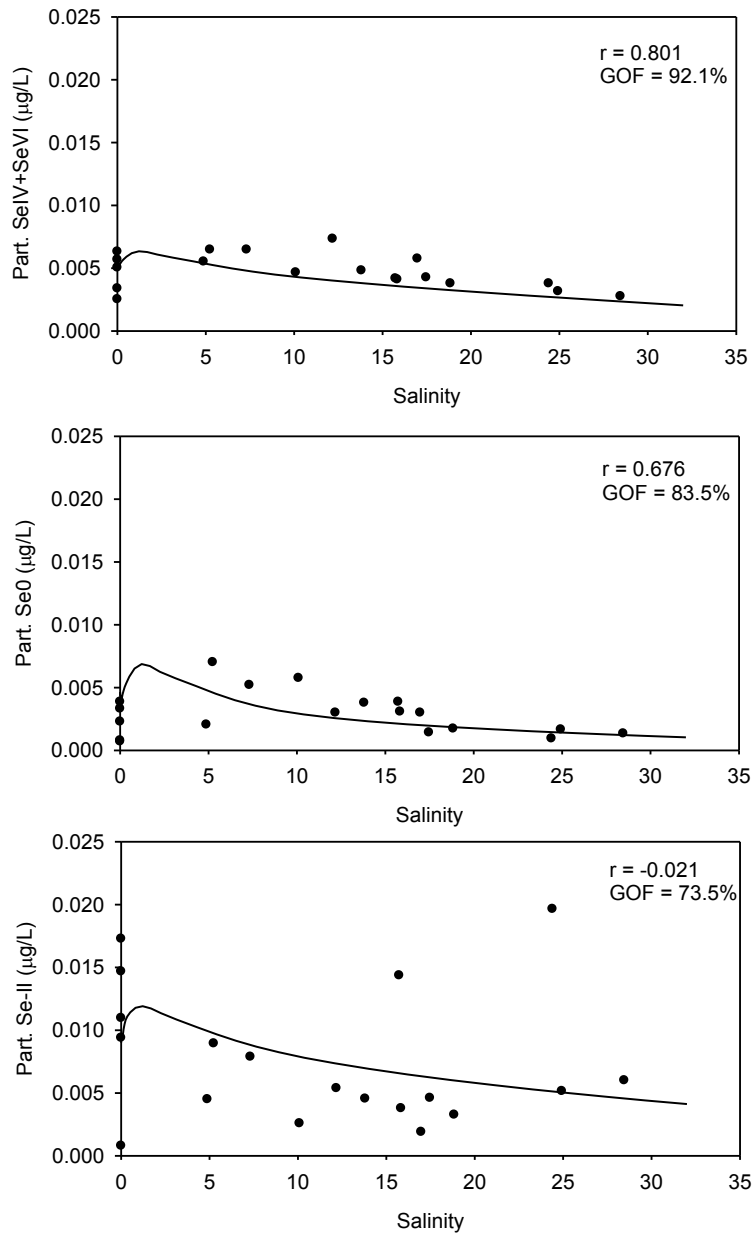


Figure 3-12 Simulated particulate selenium concentrations in different species compared to the observed data for April 1999.

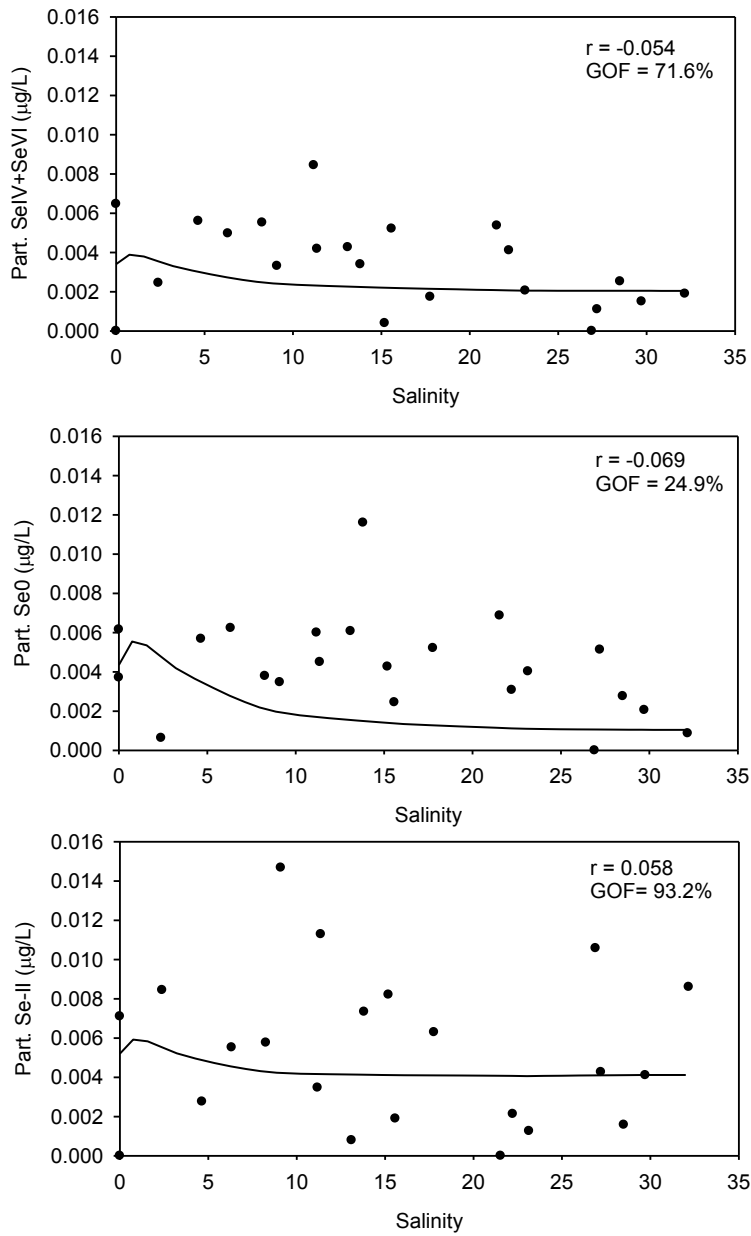


Figure 3-13 Simulated particulate selenium concentrations in different species compared to the observed data for November 1999.

Table 3-5
Comparison of predicted and observed mean salinity, TSM, chlorophyll a, selenite, selenate, organic selenide, particulate organic selenide, particulate adsorbed selenite + selenate, and particulate elemental selenium and percent error for calibration period of 1999

Parameter	Units	Predicted	Observed	Percent Error (%)
Salinity	Psu	13.153	14.272	-7.84
TSM	mg/L	0.023	0.024	-4.17
Chlorophyll a	µg/L	2.67	3.15	-15.24
SeIV	µg/L	0.016	0.015	6.67
SeVI	µg/L	0.053	0.06	-11.67
OrgSe	µg/L	0.029	0.033	-12.12
POrgSe	µg/L	0.008	0.008	0.00
Pseivvi	µg/L	0.004	0.003	33.33
PSe0	µg/L	0.003	0.003	0.00

3.3. MODEL EVALUATION

Because the model calibration was performed for only one year (1999), model evaluation against other time periods with different flow conditions is necessary. Model evaluation was performed using data for 1986 and for years after 1999. Calibration using both 1999 and 2001 data does not show significant changes in calibrated parameters for salinity and phytoplankton. However after 1999, detailed selenium concentration data by species are not available. The only data available are the total selenium concentration data collected by Regional Monitoring Program (RMP; http://www.sfei.org/rmp/rmp_data_access.html).

3.3.1 Evaluation of Salinity, TSM, Phytoplankton and Selenium for Individual Sampling Dates in 2001 and 2005

The calibrated model was evaluated against estuarine profile data for salinity, TSM, and phytoplankton for water year 2001 and 2005 collected by USGS, and long-term total selenium data collected by RMP for water year 2001 through water year 2005. Of these limited additional years of sampling, our goal was to select wet and dry years for comparison to the 1999 calibration year. Water year 2001 was selected because it was a dry year, with flows much lower than 1999 and water year 2005 was selected because it was a relatively wet year based on the classification from DWR (<http://cdec.water.ca.gov/cgi-progs/iodir/WSIHIST>). More specifically, 2001 was classified as a dry year for both the Sacramento and San Joaquin River basins, and 2005 was classified as an above normal year for the Sacramento basin and a wet year for the San Joaquin basin.³ No critically dry years occurred during the 2001-2005 period. The evaluation was for both simulations along the estuary longitude for various sampling time periods and simulations at fixed locations over

³ In summary, the water year (October 1 to September 30) discharges for 1999, 2001, and 2005, in million acre-feet, were as follows:

	1999	2001	2005
Sacramento River Basin	21.19	9.81	18.55
San Joaquin River Basin	5.91	3.18	9.21

long-term time periods, for both physical and biological parameters and selenium concentrations.

Time periods of model calibration/evaluation are shown in Figure 3-14. The calibration dates for physical parameters have a flow range of 150-1,425 m³/s, which contains the range of flows used for the evaluation period (Figure 3-14).

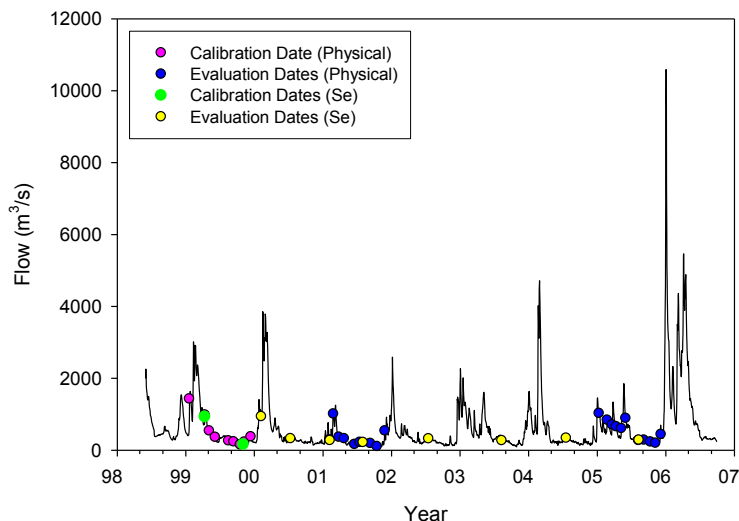


Figure 3-14 Dates for model calibration and evaluation for various parameters.

Evaluation of salinity for the low flow year 2001 suggested good agreement of simulated salinity versus observed values for different months across the year. The salinity was over-predicted or under-predicted for a few high flow months. However, overall values for goodness of fit for these months are between 71.5-97.9% (Figure 3-15). Evaluation of TSM against the observed values for the low flow year 2001 also suggested good agreement between the observed and simulated values (GOF = 36.4 – 99.4%) (Figure 3-16). The location of estuarine turbidity maximum (ETM) was simulated well for most months in 2001, particularly for June and July 2001. TSM was under-predicted occasionally, similar to the pattern in model performance for the calibration period. The under-prediction in ETM may result in higher predicted selenium content on particulates.

Evaluation of simulated chlorophyll a concentrations for 2001 against the observed values indicated that the mean values of chlorophyll a concentrations were predicted well in the estuary for most months (Figure 3-17; GOF = 53.7 – 95.7%). For about two months, chlorophyll a concentrations were under predicted near the Central Bay, similar to the pattern in the calibration. For the evaluation period, simulated correlation coefficient (r) is 0.92-1.00 for salinity in 2001, 0.68 – 0.97 for TSM in 2001, and 0.02-0.79 for chlorophyll a in 2001. Chlorophyll a concentrations in 2001 do not show a peak in the upper estuary as shown in the calibration period therefore the simulated concentrations compared well with the observed values for that region.

Evaluation of salinity for above normal flow year 2005 showed very good agreement with the observed data (Figure 3-18; GOF = 50.4 – 99.7%). The evaluation of TSM for 2005

shows good agreement for the first several months, particularly for January, March and June 2005 (Figure 3-19). For April and May 2005, the ETM was under-predicted (Figure 3-19; GOF = 48.2 – 97.7%). This is similar to the results in calibration where ETM was under-predicted in some occasions.

Currently salinity is simulated using a constant K_w overtime for the validation period of 2000-2006. Alternatively K_w can be simulated as a function of flow and salinity in the estuary, as in Harris and Gorley (1998). The results in salinity are very similar to current results reported, with slightly lower goodness of fit. Alternatively, salinity could also be simulated as a function flow, salinity and salinity gradient, as in Meseck (2002). The results are a better ETM in TSM simulation for high flow months (particularly for June 1999), however also predicts ETMs in TSM for months without observed ETM. The formulation also results in a relatively linear predicted salinity profile along the estuary.

Evaluation of chlorophyll a for 2005 indicated that the model was able to capture chlorophyll a concentrations both temporally and spatially for most of the months (Figure 3-20; GOF = 13.5 – 98.5%). Chlorophyll a concentrations were under-predicted during spring months. The phytoplankton is simulated as light dependent. Simulated photosynthetically active radiation (PAR) that affects phytoplankton growth is low during spring months; however, significant phytoplankton blooms still occurred during spring as shown in the observed data. The elevated phytoplankton concentrations could be due to elevated nutrient concentrations, advection from South Bay, less grazing in Central Bay, different species of phytoplankton, higher maximum photosynthesis rates, less light extinction in the Central Bay or other processes that contribute to phytoplankton bloom that are not captured by the model. Currently the model under-predicted some of these blooms during spring. Advection from South Bay was currently simulated as freshwater inflow of South Bay multiplied by a chlorophyll a concentration of 6 $\mu\text{g/L}$. Phytoplankton concentrations as shown in Section 4 affect selenium concentrations in particulates and therefore in bivalves. The under-prediction could potentially result in under-prediction of selenium content on particulates. For 2005, peaks in chlorophyll a concentrations in the upper estuary were not observed, as opposed to patterns shown in the calibration period.

For the evaluation period, the correlation coefficient r is 0.92 – 1.00 for salinity in 2005, 0.09-0.94 for TSM, and -0.64 – 0.85 for chlorophyll a. Correlation between predicted and observed salinity, TSM and chlorophyll a concentrations for 2001 and 2005 is shown in Figure 3-21. The correlation between predicted and observed values was reasonable. For the evaluation period, some adjustments in zooplankton grazing rates were still needed to better simulate variations in phytoplankton concentrations.

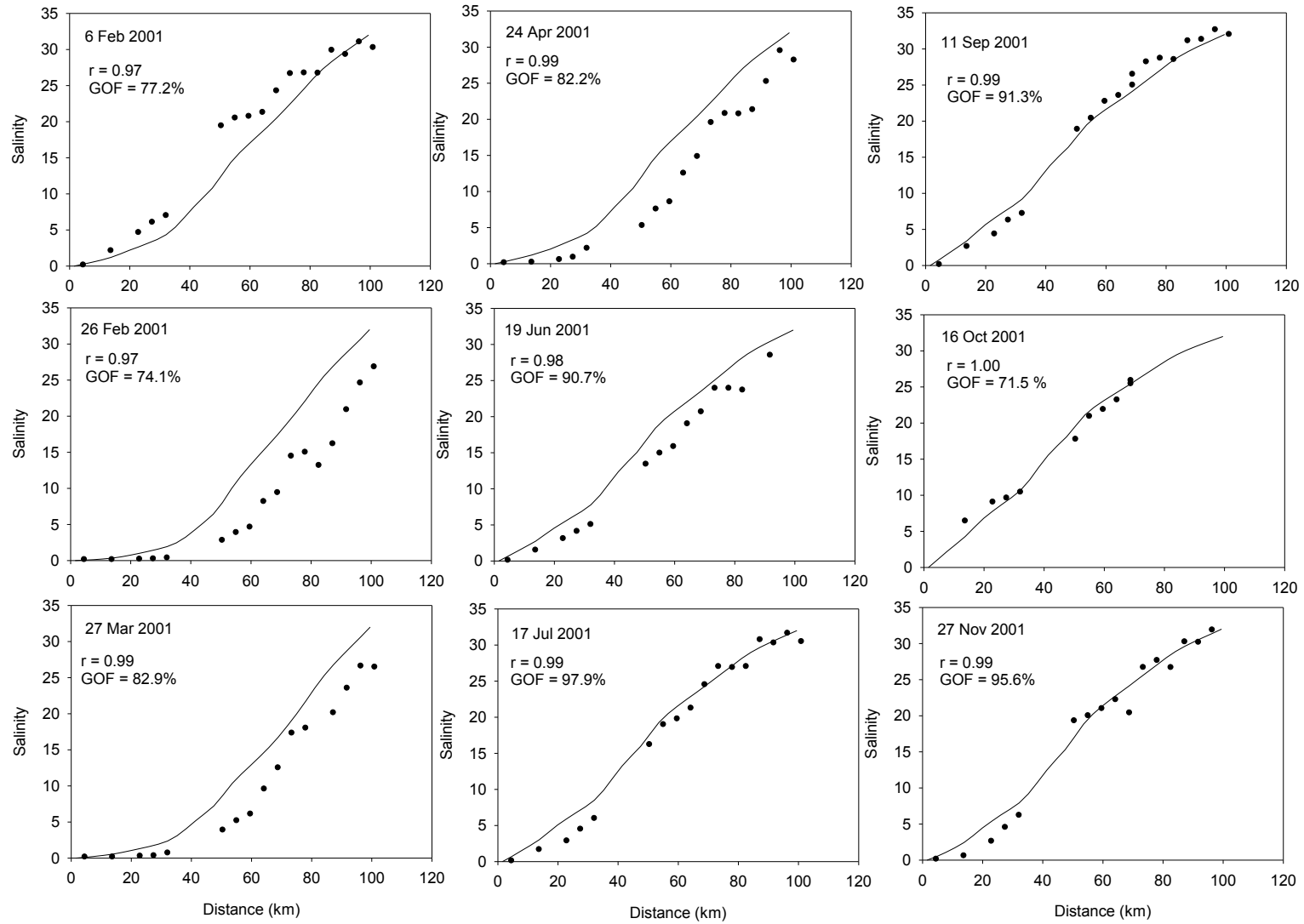


Figure 3-15 Evaluation of simulated monthly salinity profiles for a low flow year 2001 (Data source: USGS)

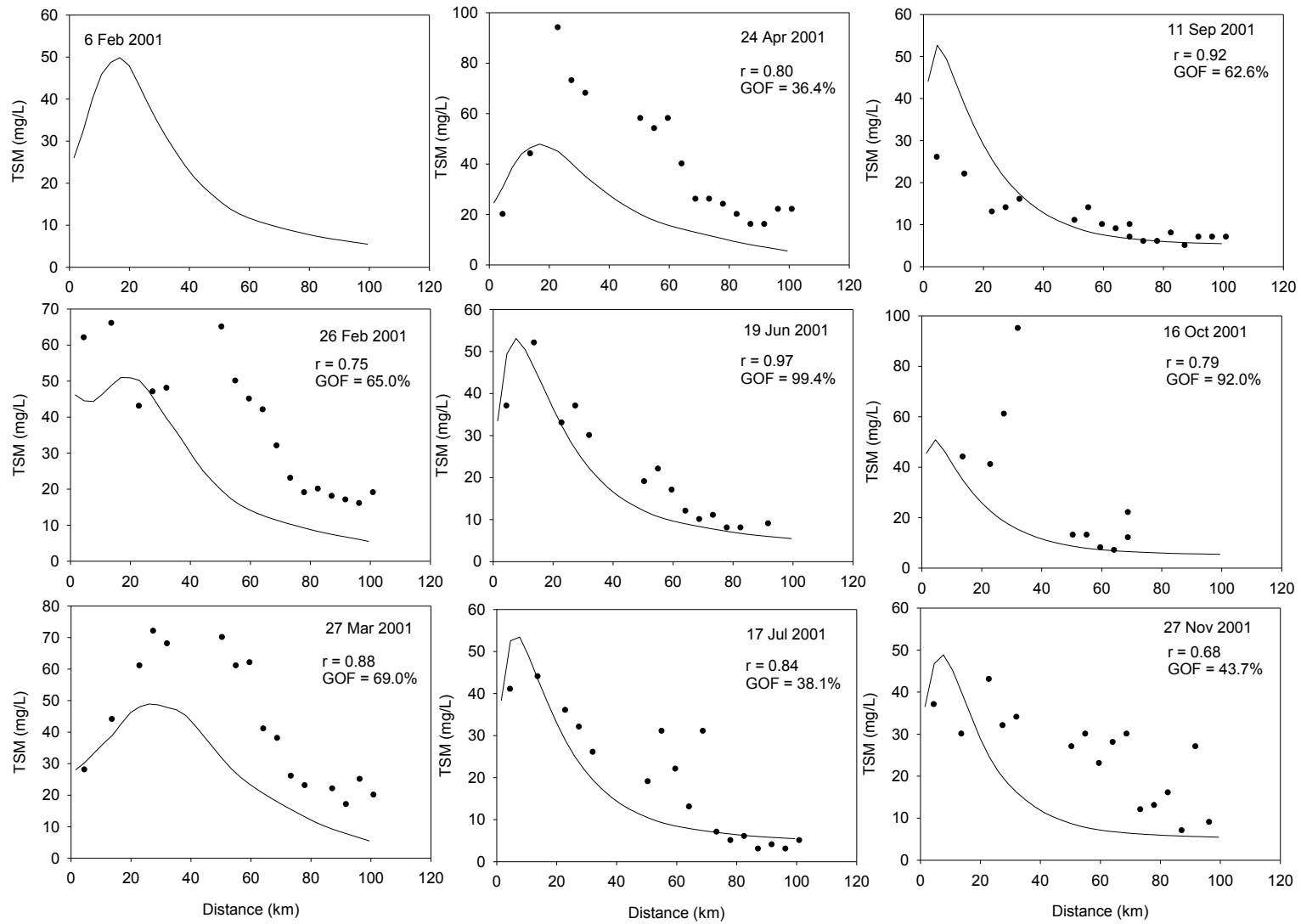


Figure 3-16 Evaluation of simulated monthly TSM profiles for a low flow year 2001 (Data source: USGS).

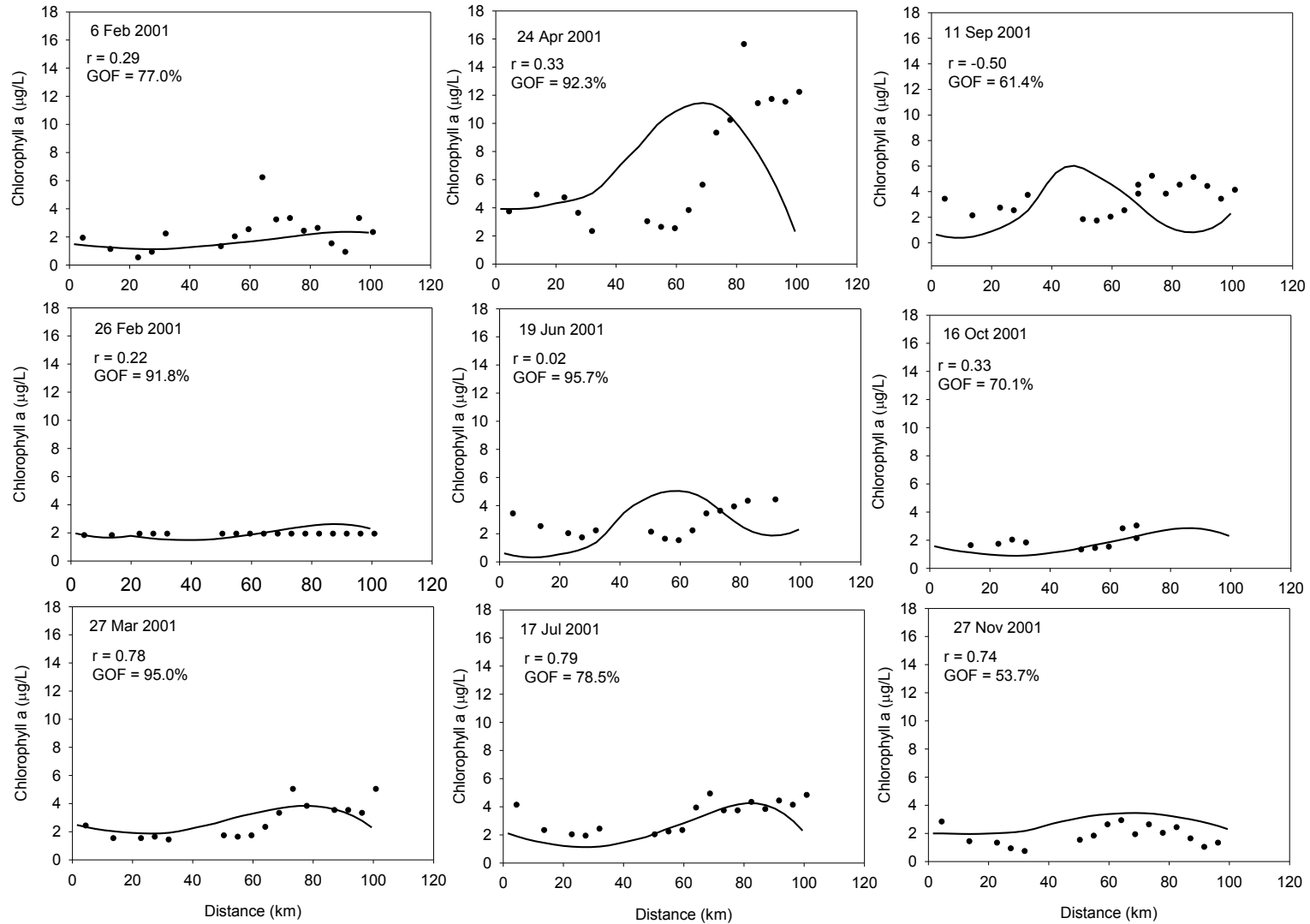


Figure 3-17 Evaluation of simulated monthly chlorophyll a concentrations for a low flow year 2001 (Data source: USGS).

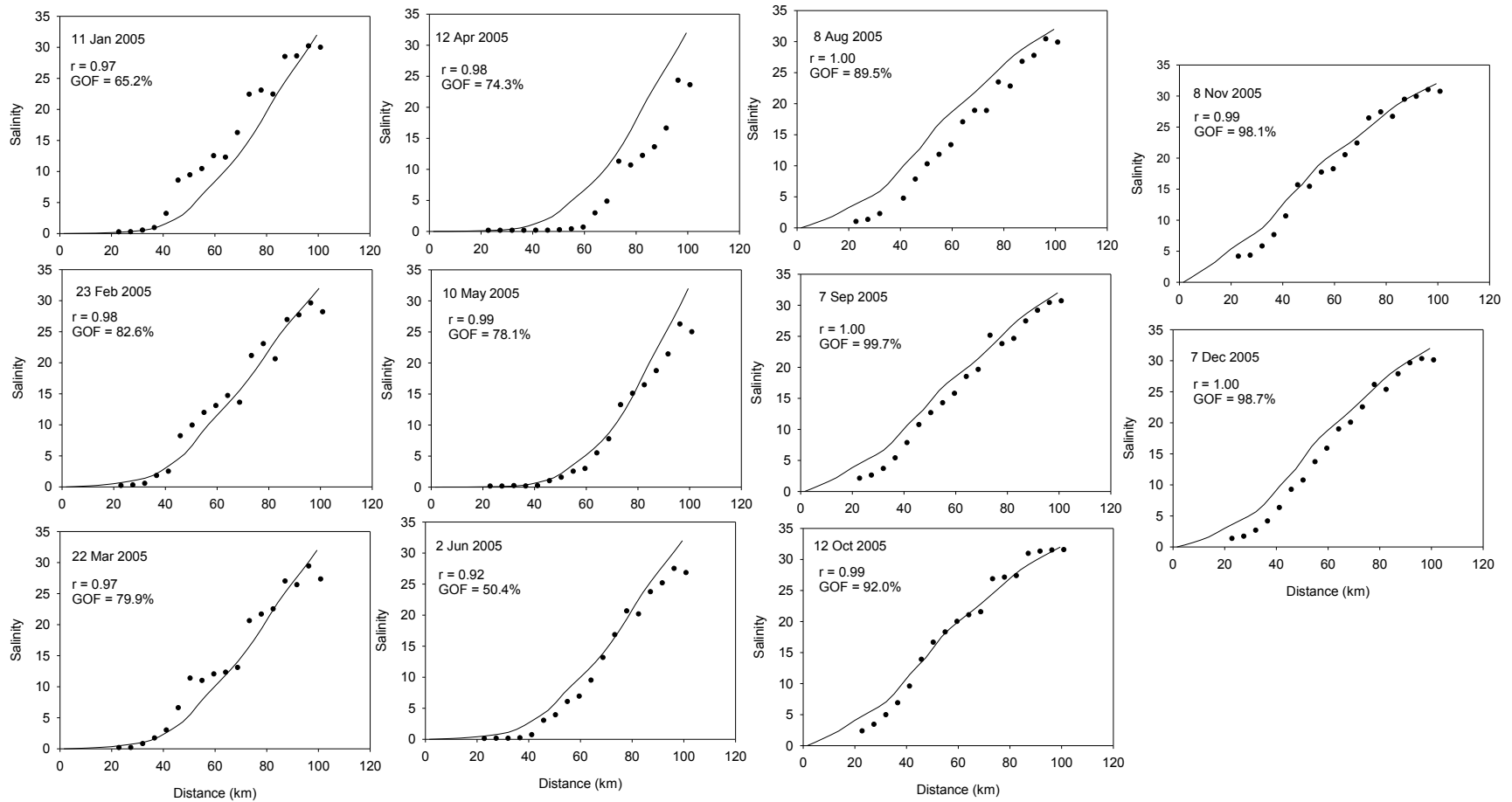


Figure 3-18 Evaluation of simulated monthly salinity profiles for a high flow year 2005 (Data source: USGS).

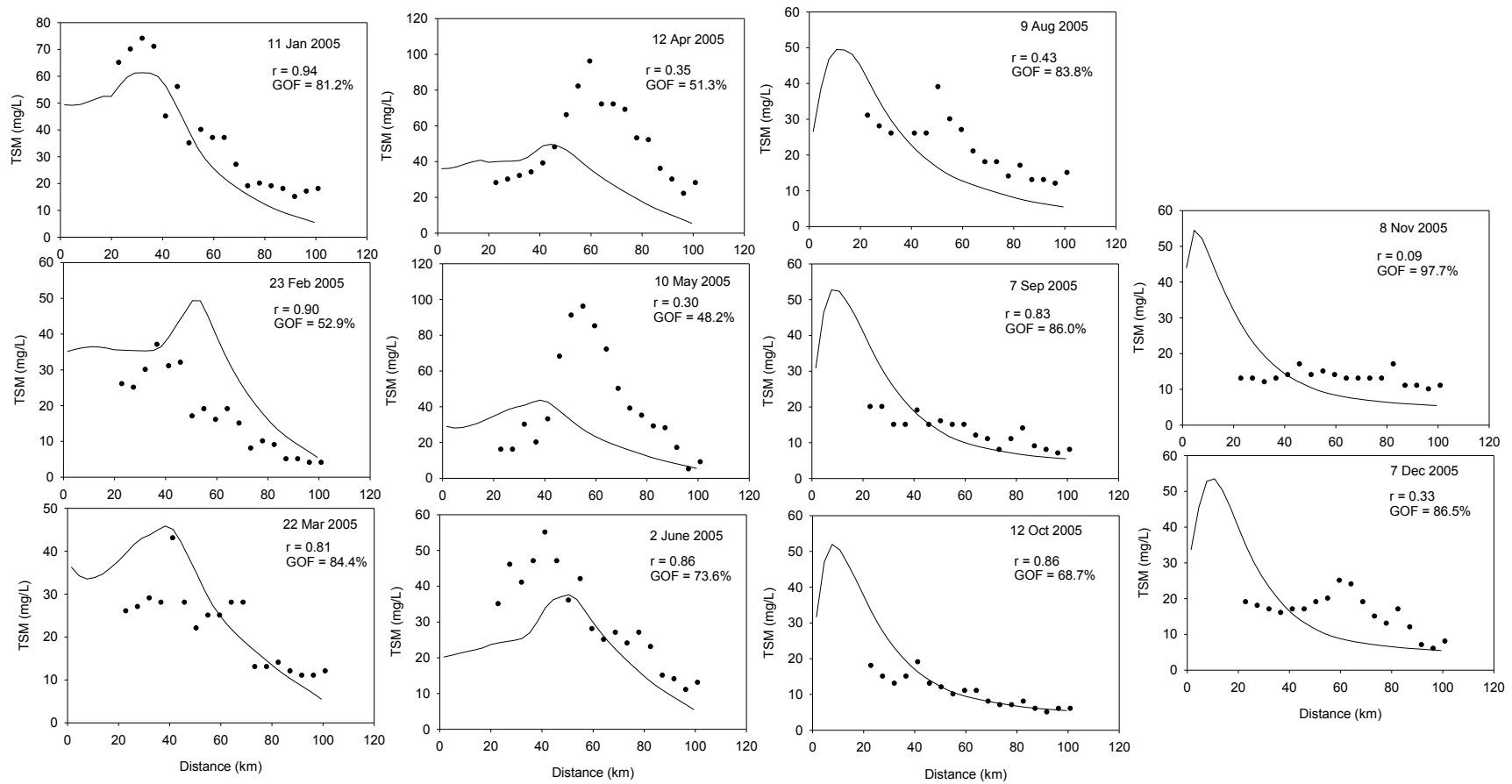


Figure 3-19 Evaluation of simulated monthly TSM profiles for a high flow year 2005 (Data source: USGS).

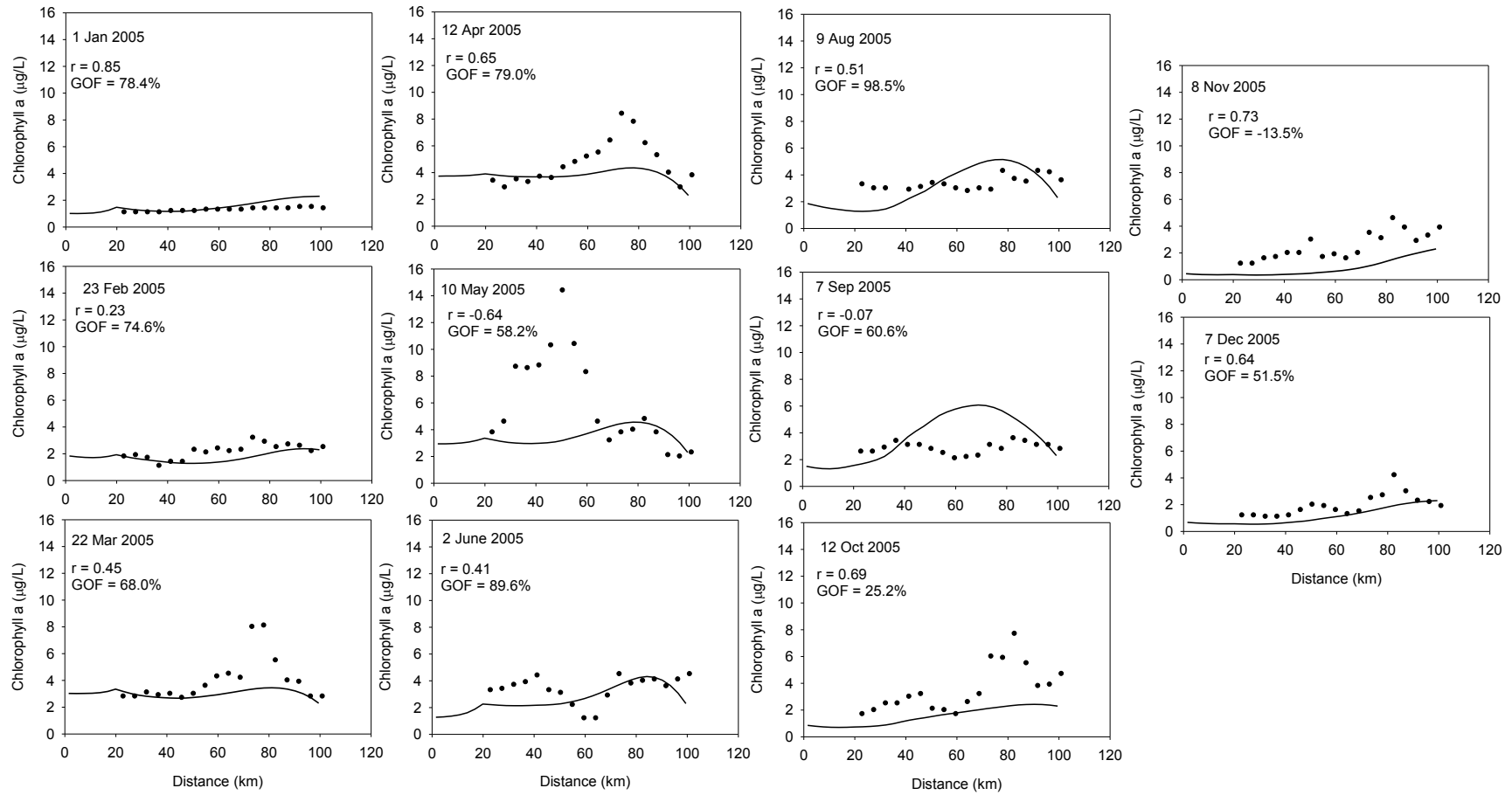


Figure 3-20 Evaluation of simulated monthly chlorophyll a concentration profiles for a high flow year 2005 (Data source: USGS).

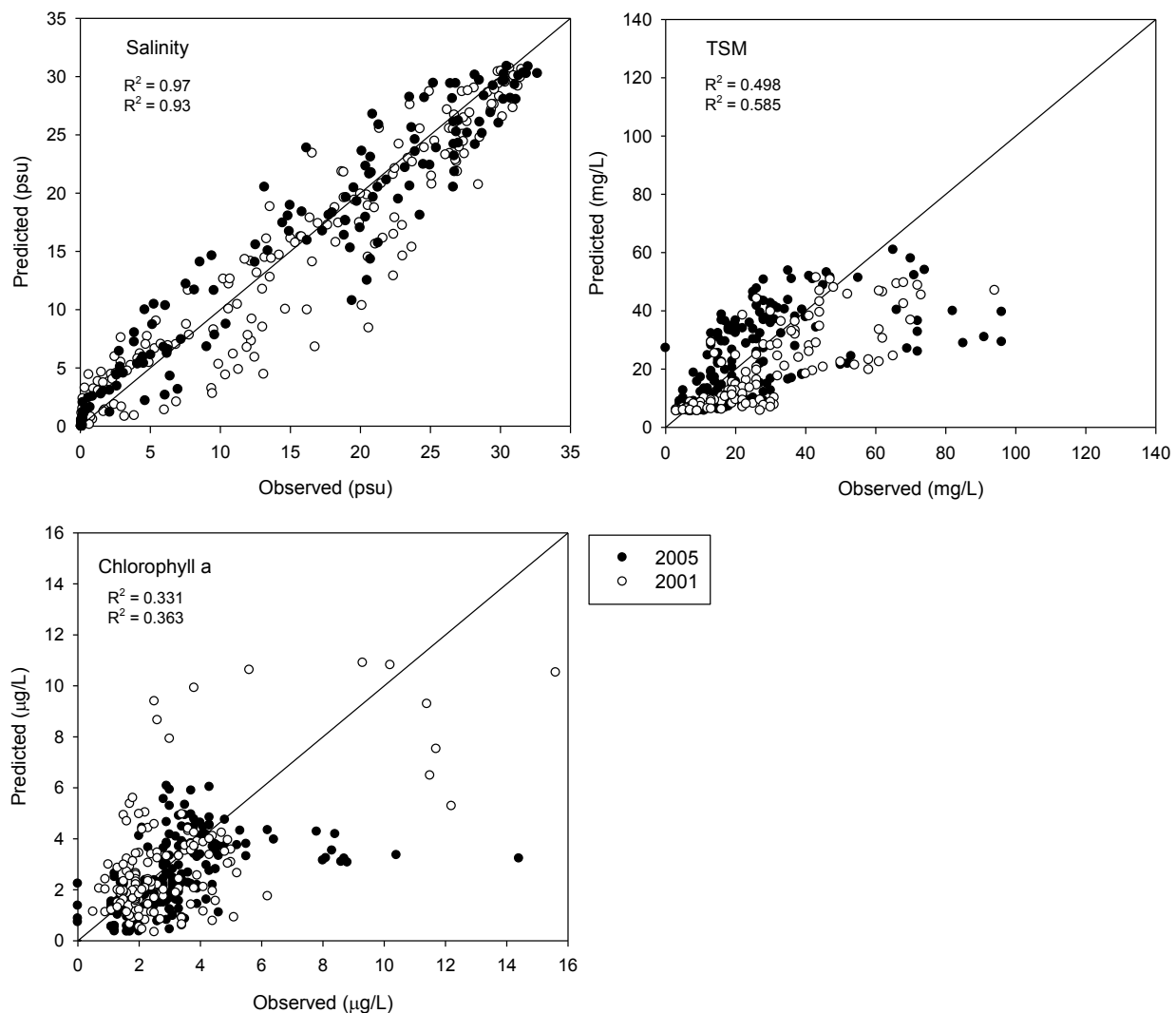


Figure 3-21 Model simulated salinity, TSM, and chlorophyll a concentrations for 2001 and 2005 compared to the observed values.

The model was run for multiple years from 2000 to 2005. Simulated model results for total selenium (particulate + dissolved) from February 2000 to August 2005 were also compared against the observed data from RMP across the estuary for multiple time periods. As noted earlier, this comparison was driven by the fact that the RMP data do not report speciated selenium concentrations. Comparison of simulated concentrations against the RMP data suggested that the model is able to simulate selenium concentrations well for a range of hydrological and load input conditions during 2000-2005, including both dry year and wet year flows, and dry season and wet season conditions (Figure 3-22). The simulation years are mostly for years after refinery clean-up, which occurred in mid-1998, and the mid-estuarine selenium peak is not very evident for most of the years simulated. Although the inter-annual variations in total selenium data are significant, simulated total selenium concentrations were generally in the range of the observed concentrations.

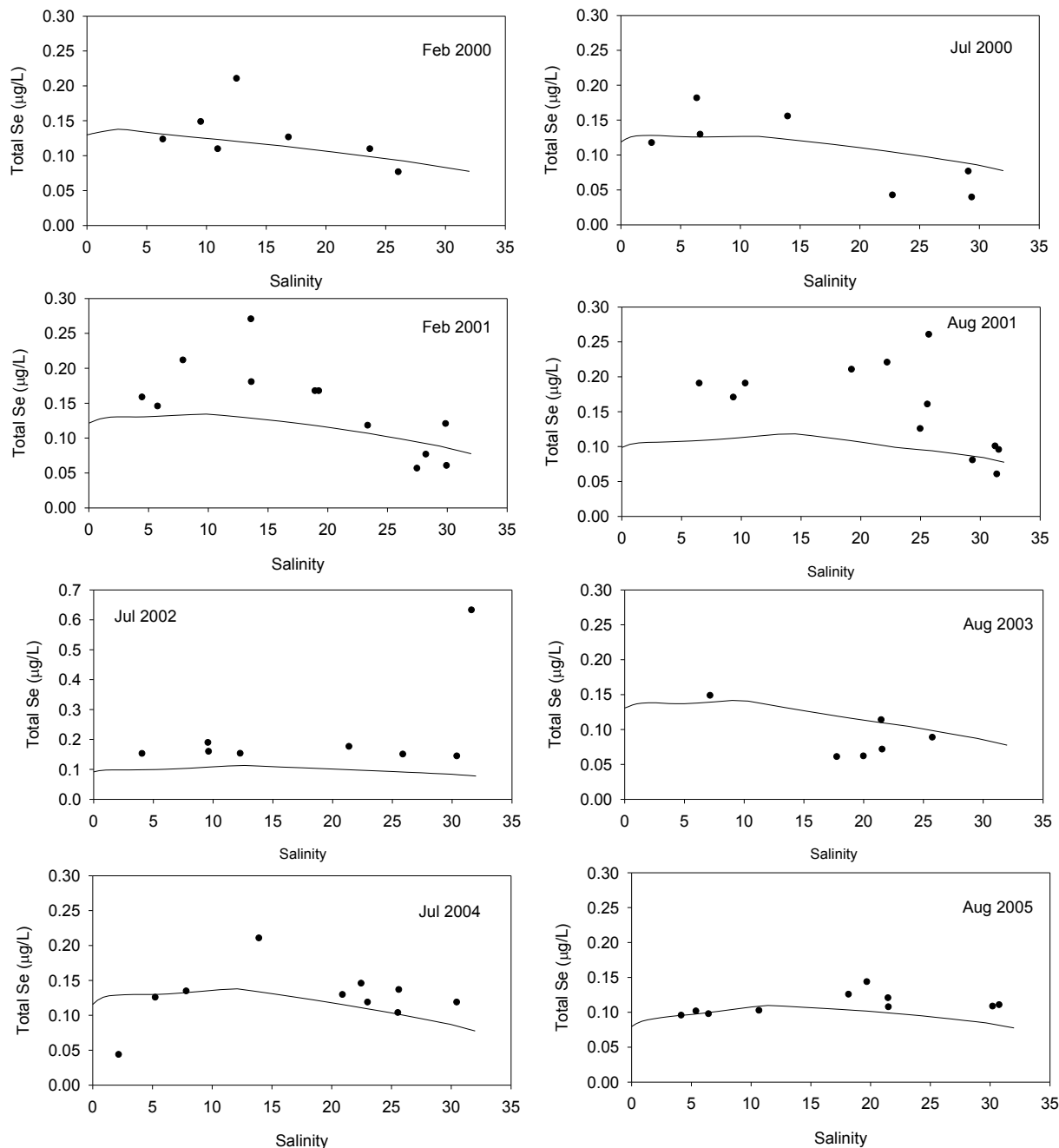


Figure 3-22 Model simulated total selenium concentrations (dissolved + particulate) compared to selenium data collected by RMP. Note that the RMP dataset does not report selenium species information.

3.3.2 Long-term Evaluation of TSM and Chlorophyll a Concentrations

Simulated TSM and chlorophyll a concentrations were also evaluated against data from the USGS long-term monitoring stations. The model-simulated chlorophyll a and TSM concentrations were evaluated against long-term data at four stations, station 3 (Suisun Bay), 6 (Suisun Bay), 14 (San Pablo Bay) and 18 (Central Bay), respectively. The model is able to capture the seasonal patterns in chlorophyll a concentrations and TSM (Figure 3-23 and

Figure 3-24) relatively well. The model is able to capture the peaks and lows in both TSM and chlorophyll a concentrations.

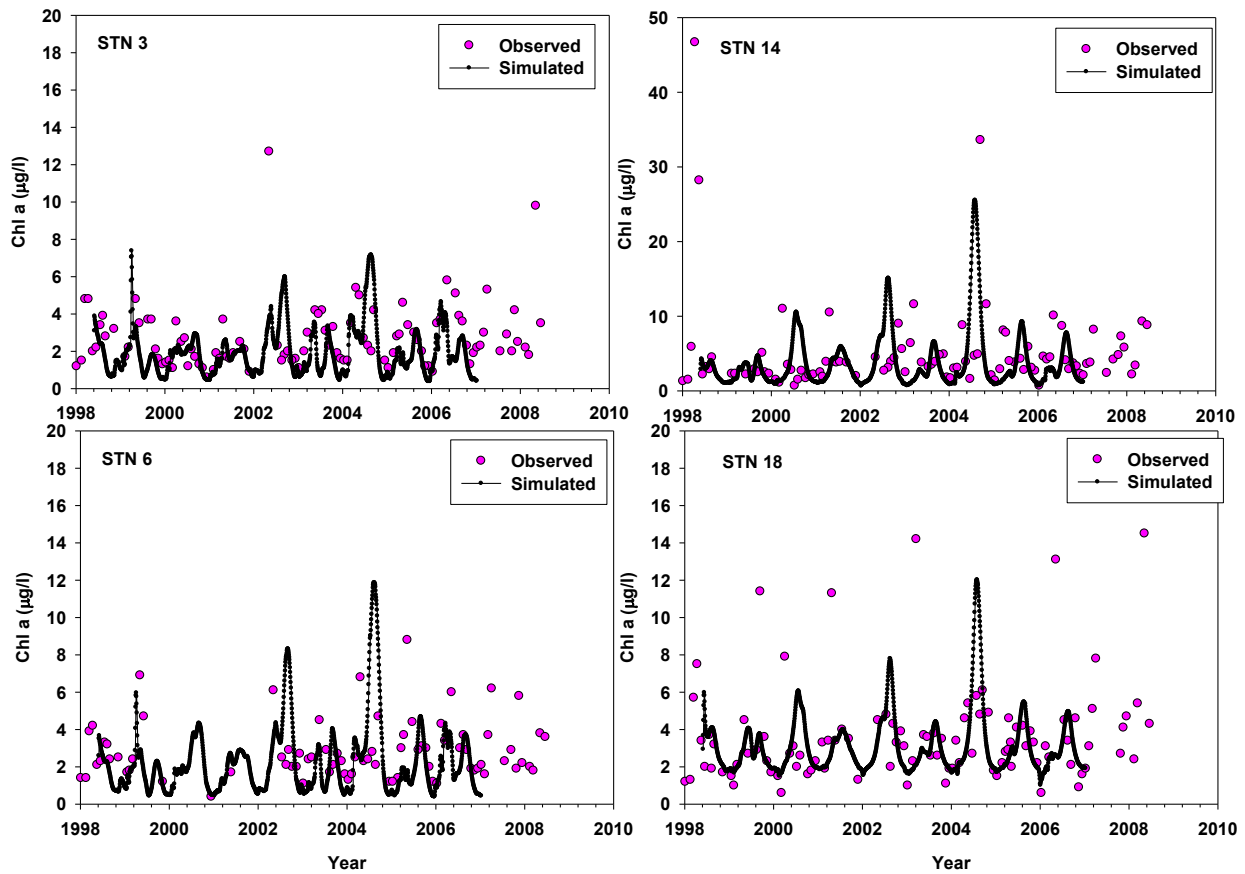


Figure 3-23 Simulated time series of phytoplankton concentrations compared to observed data from USGS at stations 3 (Suisun Bay), 6 (Suisun Bay), 14 (San Pablo Bay) and 18 (Central Bay). Locations of USGS stations are shown in Figure 1-2.

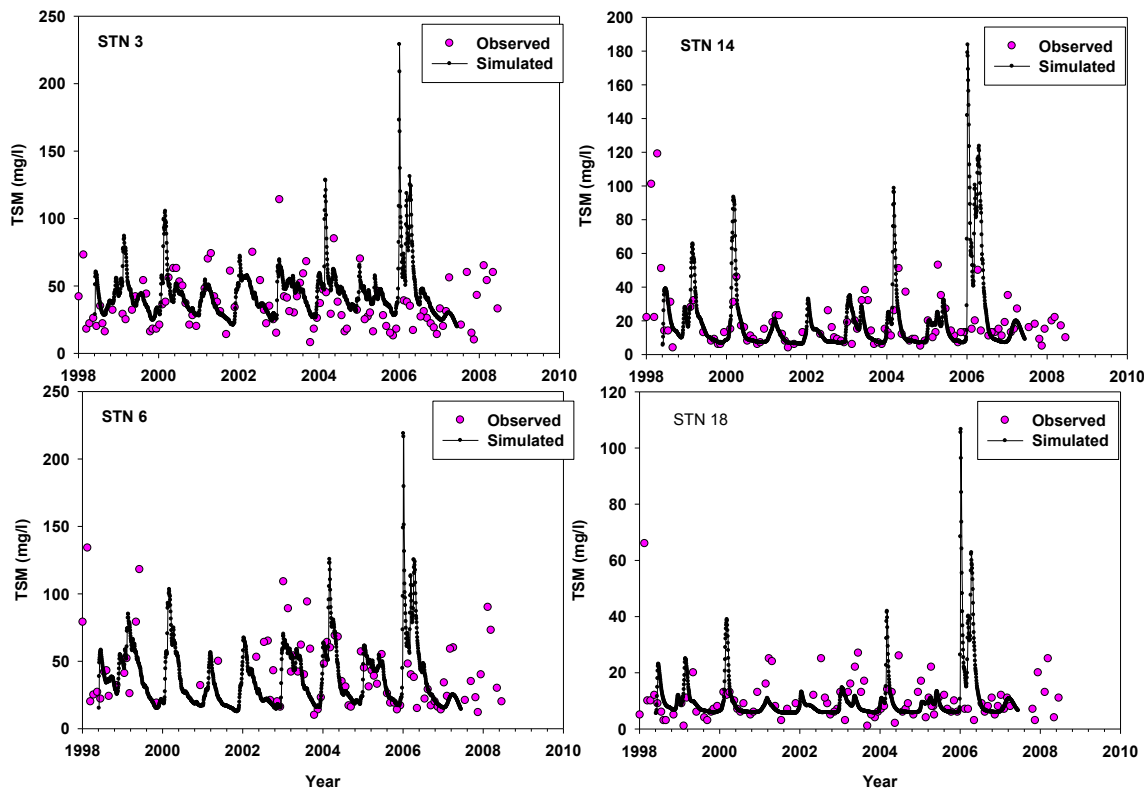


Figure 3-24 Simulated time series of TSM compared to observed data from USGS at stations 3 (Suisun Bay), 6 (Suisun Bay), 14 (San Pablo Bay) and 18 (Central Bay).

3.3.3 Evaluation of Long-term Selenium Concentrations

Simulated dissolved selenium concentrations were also evaluated against the long-term record for several long-term RMP monitoring stations BF10 (Pacheco Creek) in Suisun Bay, BF 20 in Suisun Bay, BD30 (Pinole Point) in San Pablo Bay and BC10 in Central Bay (Figure 3-25). The results generally show good agreement between model simulated total selenium concentrations (particulate + dissolved) and the observed data for the simulation period of 1999-2006. Higher total selenium concentrations were observed for periods prior to the improved wastewater treatment from refineries. Selenium loads for this period (prior to 1999) should be greater than currently used in the model for 1999 onward. Some high total selenium concentrations in Suisun Bay are not captured well by the model. This may be due to variations in selenium inputs from rivers or tributaries or local-scale processes that are not represented well by the model. For San Pablo Bay, the observed variation in total selenium concentrations along the estuary is captured well by the model prediction. The Central Bay showed less variation both in observed and predicted values. The predicted variation is most likely due to variations in load inputs, particularly from tributaries and the Delta as shown in the previous section (Figure 2-15 and Figure 2-18).

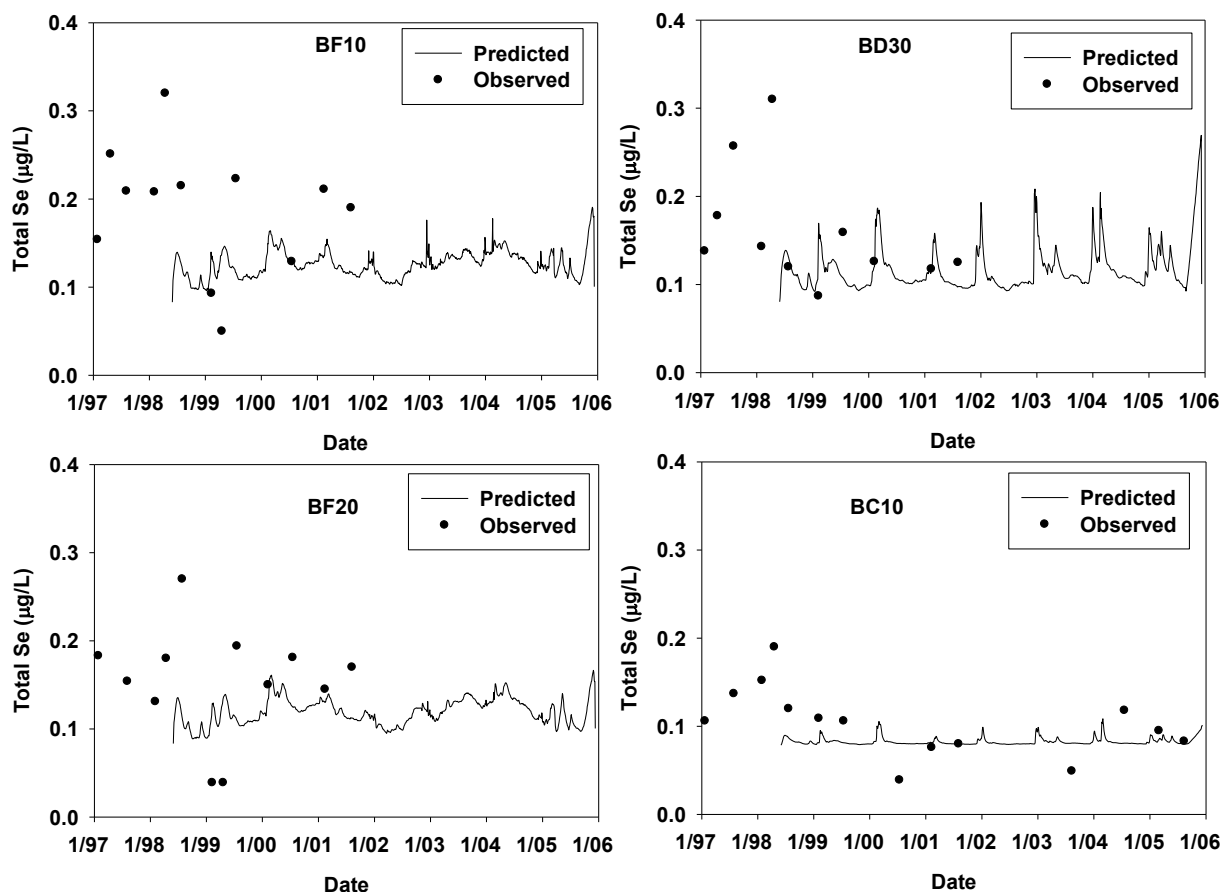


Figure 3-25 Model simulated total selenium concentrations at BF10 (Suisun Bay), BF20 (Suisun Bay), BD30 (San Pablo Bay) and at BC10 (Central Bay) compared to observed total selenium by RMP.

3.3.4 Model Predicted Particulate Selenium Concentrations

Simulated selenium concentrations on particulate matter (in $\mu\text{g/g}$) for November 11, 1999 were comparable to the observed data from Doblin et al. (2006; Figure 3-26). Particulate selenium is not directly measured by RMP. The predicted mean particulate selenium concentrations for NSFB for November 11, 1999 is $0.77 \pm 0.35 \mu\text{g/g}$, compared well to the observed value of $0.735 \pm 0.25 \mu\text{g/g}$ ($r = 0.45$). The model-predicted upper-bound and lower-bound of the particulate selenium concentration is also shown. The upper-bound and lower-bound constituent values are derived by including an upper-bound and a lower-bound of several affecting parameters (derived in calibration), including selenium content on particulates at the head of estuary and San Joaquin load removal constants. The range of concentrations shown here suggests a relatively narrow range of uncertainties in parameter estimates.

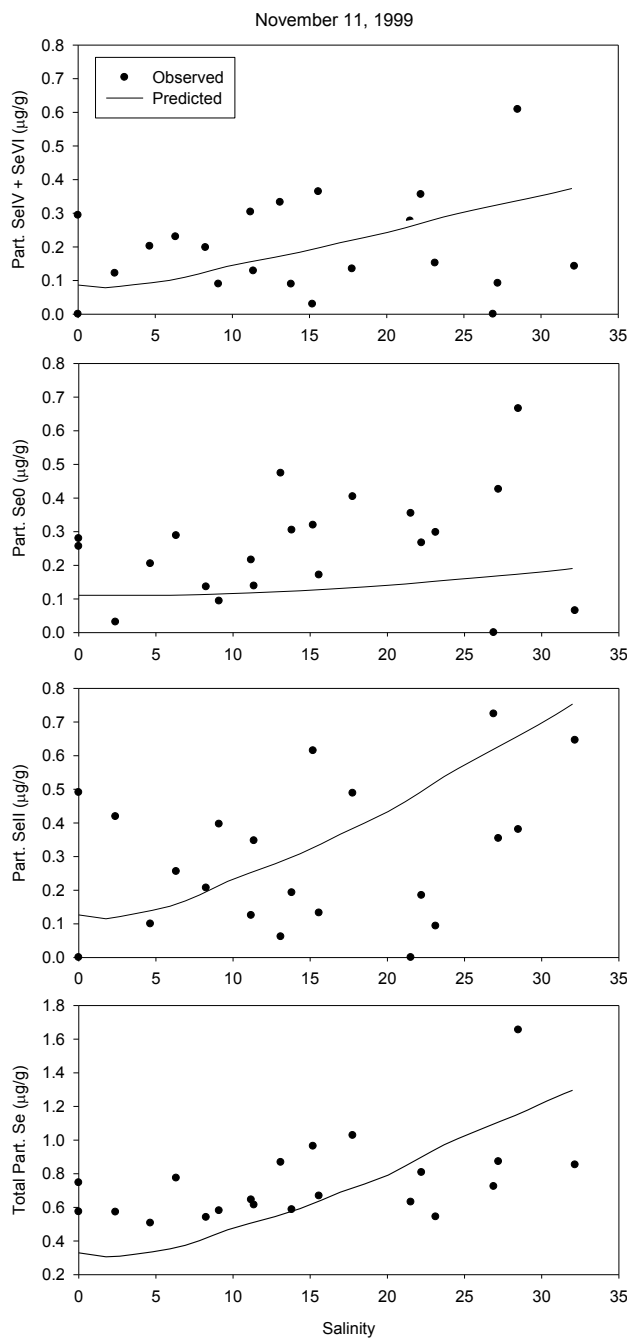


Figure 3-26 Simulated particulate selenium compared with the observed data from Doblin et al. (2006) for November 1999. The lowermost plot shows the range of particulate Se predictions using the high and low values of related calibration parameters.

Model simulated particulate selenium (in $\mu\text{g/g}$) and dissolved selenium (in $\mu\text{g/L}$) can be used to estimate the partition coefficients (K_d). Note that these are not true equilibrium partition coefficients in that the model uses a dynamic formulation for dissolved-particulate exchange; however, the instantaneous ratios of particulate and dissolved selenium, approximated as K_d , can be useful for comparing against the large amount of data from other systems where partition coefficients are reported. K_d values estimated in this work range

over an order of magnitude depending on the time and location of calculation. The variation is reflective of the changing sources and speciation of particulate selenium in the bay over time. Estimated K_d values range from 2.0×10^3 L/kg to 1.0×10^4 L/kg for a location in the San Pablo Bay (close to STN 14) for 1999 and from 2.73×10^3 and 1.72×10^4 L/kg as a function of distance for a low flow period (November 11, 1999; Figure 3-27). These ranges are in the range of K_d values summarized by Presser and Luoma (2006) for various ecosystems and the water column in Bay-Delta system (Table 3-6). However, the order-of-magnitude variability indicates the difficulty of using a single K_d value to accurately represent particulate concentrations over a range of conditions in the bay.

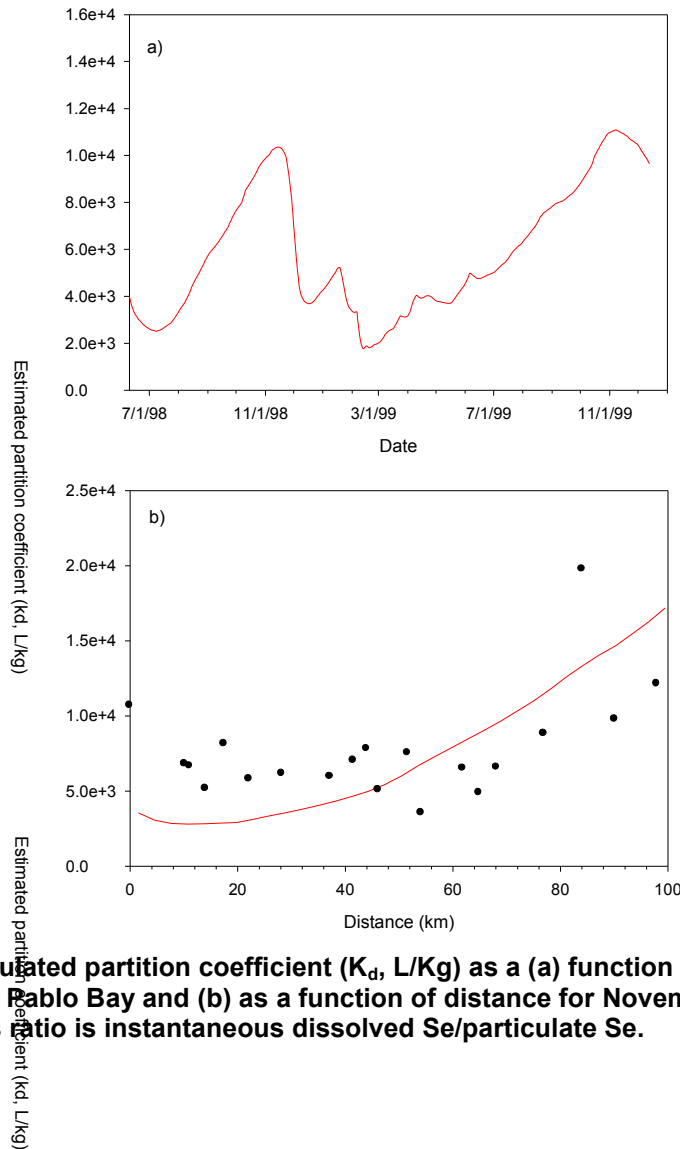


Figure 3-27 Simulated partition coefficient (K_d , L/Kg) as a (a) function of time for year 1999 in San Pablo Bay and (b) as a function of distance for November 11, 1999. The Y axis ratio is instantaneous dissolved Se/particulate Se.

Table 3-6
Partitioning Coefficients (K_d) Between Dissolved Selenium and Particulate Selenium in the Literature and Ssimulated by the Model (after Luoma and Presser, 2006)

Ecosystem or Organism	Selenium			Reference
	Dissolved (µg/L)	Particulate (µg/g)	Distribution coefficient, L/kg (K _d)	
Kesterson Reservoir Pond 2 Terminal Pond	330 14	55-165 13-24	0.2 -0.5 × 10 ³ 0.9 -1.7 × 10 ³	Presser and Piper (1998) Presser and Barnes (1998)
Belews Lake	~11	~15	1.3 × 10 ³	Lemly (1995)
Benton Lake Pool 1 channel Pool 2 Pool 5	4 10.4 0.74	10 3.5 0.35	2.5 × 10 ³ 0.34 × 10 ³ 0.5 × 10 ³	Zhang and Moore (1996)
Constructed wetland	5.0-9.8	2.1-6.7	0.2 -1.2 × 10 ³	Hansen et al. (1998)
San Luis Drain	330	84	0.25 × 10 ³	Presser and Piper (1998)
Grassland Bypass Channel Project	62.5	30	0.5 × 10 ³	Presser and Luoma (2006)
Delaware River (tidal freshwater)	0.17-0.35	0.6-1.5	4 × 10 ³	Riedel and Sanders (1998)
Diatoms	-	-	1.1 × 10 ⁵	Reinfelder and Fisher (1991)
Dinoflagellates	-	-	4 × 10 ³	Reinfelder and Fisher (1991)
Great Marsh, Delaware	0.01-0.06	0.3-0.7	3 × 10 ³ -1 × 10 ⁴	Velinsky and Cutter (1991)
San Francisco Bay-Delta (suspended particulate matter, 1986, 1995, 1996)	0.1-0.4	1-8	1-4 × 10 ⁴	Cutter and cutter (2004) Doblin et al. (2006)
San Francisco Bay Delta sediment	0.1-0.3	0.2 – 0.5	1-5 × 10 ³	Johns et al. (1988)
San Pablo Bay (1999)	0.076-0.119	0.318-1.317	2.81 × 10 ³ – 1.72 × 10 ⁴	This model
Estuary profile (Nov 11, 1999)	0.078-0.212	0.344-1.299	1.77 × 10 ³ – 2.67 × 10 ⁴	This model

3.3.5 Summary of Model Evaluation

The evaluation process for both short-term (individual sampling dates along the salinity profile) and long-term periods (limited number of fixed locations with multiple years of data) suggests that the model is able to reproduce spatial variation and time trends in several major parameters. Salinity profiles for individual sampling dates, representing different flow conditions, are simulated very well by the model. Evaluation against the long-term record for selected water quality measures suggests seasonal trends in TSM and phytoplankton are

simulated well by the model, although occasional peaks in both parameters are not captured. Model evaluation for selenium concentrations against RMP data for both the short-term and long-term showed that simulated selenium concentrations generally fell within the range of the observed values, although the quality of the fit was not as good as for salinity.

The evaluation against new data under different hydrologic conditions, as shown here, suggests that processes that affect solutes and particulate transport as well sources of phytoplankton, TSM, and selenium are generally well-represented in the model, albeit peak concentrations are not always predicted. The limited ability to capture peak concentrations may be related to the 1-D formulation of the model, which is inherently limited in representing three-dimensional processes.

3.4. PREDICTED SELENIUM CONCENTRATIONS IN BIVALVES, FISH AND BIRDS

Model-predicted selenium concentrations in bivalves (*Corbula amurensis*) for November 11, 1999 were $9.77 \pm 4.87 \mu\text{g/g}$ compared to observed values reported by Stewart et al. (2004; $11 \mu\text{g/g}$), using an ingestion rate of 0.45 g/day and assimilation efficiency of 0.20 (elemental), 0.45 (adsorbed selenite) and 0.80 (organic selenide).

Predicted selenium concentrations in *Corbula amurensis* near Carquinez Strait as a function of time were compared to data from Stewart et al. (2004) and are shown in Figure 3-28 for a range of ingestion rates used. Different ingestion rates of particulate selenium by *Corbula amurensis* and assimilation efficiencies for organic selenium were used in the simulation. Predicted ranges in bivalve selenium concentrations are between 2 – 22 $\mu\text{g/g}$.

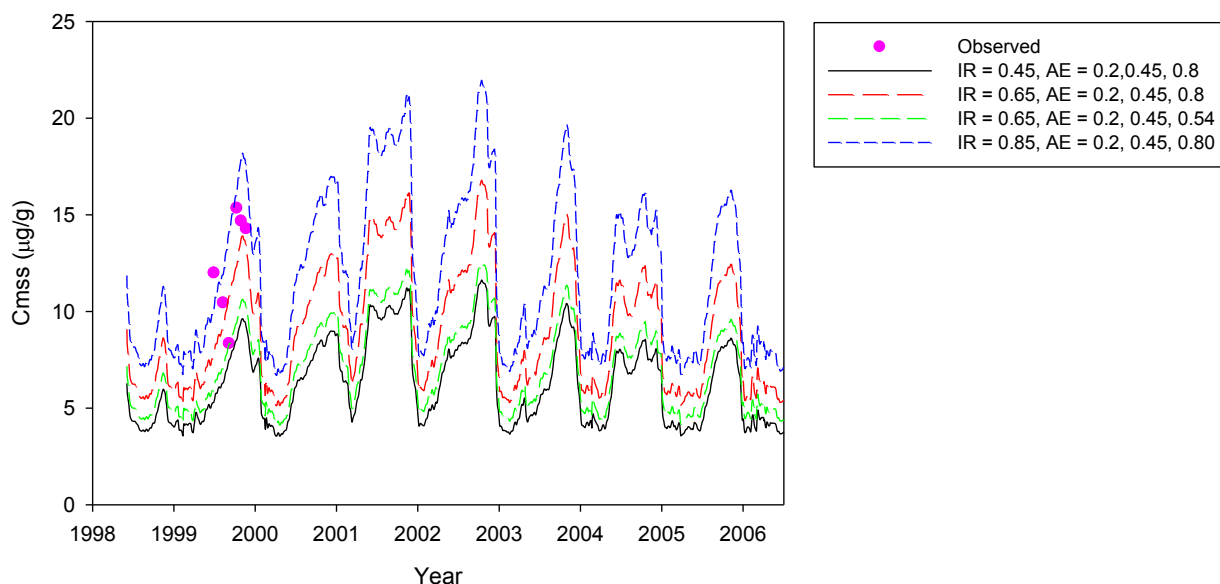


Figure 3-28 Simulated selenium concentrations in bivalve *Corbula amurensis* near the Carquinez Strait compared to observed values from Stewart et al. (2004; station 8.1). Different AEs in order are for particulate elemental selenium (AE = 0.2), particulate adsorbed selenite and selenate (AE = 0.45), and particulate organic selenium (AE = 0.80), respectively.

Simulated selenium concentrations in bivalves along the distance of the estuary were also compared to the observed data from USGS for different locations in the Bay during July 1999 to December 1999. The sampling locations by USGS are at stations 6.1, 411 and 415 in Suisun Bay, 8.1 in Carquinez Strait, and 12.5 in San Pablo Bay. The model estimates suggest that selenium concentrations in bivalves increase with the distance from the head of the estuary, although the data are only weakly supportive (Figure 3-29). The data shown are for a fairly limited period and limited spatial extent, and highlight the need for model comparisons with more recent data as well as data at higher salinities (all the way from San Pablo Bay to Golden Gate).

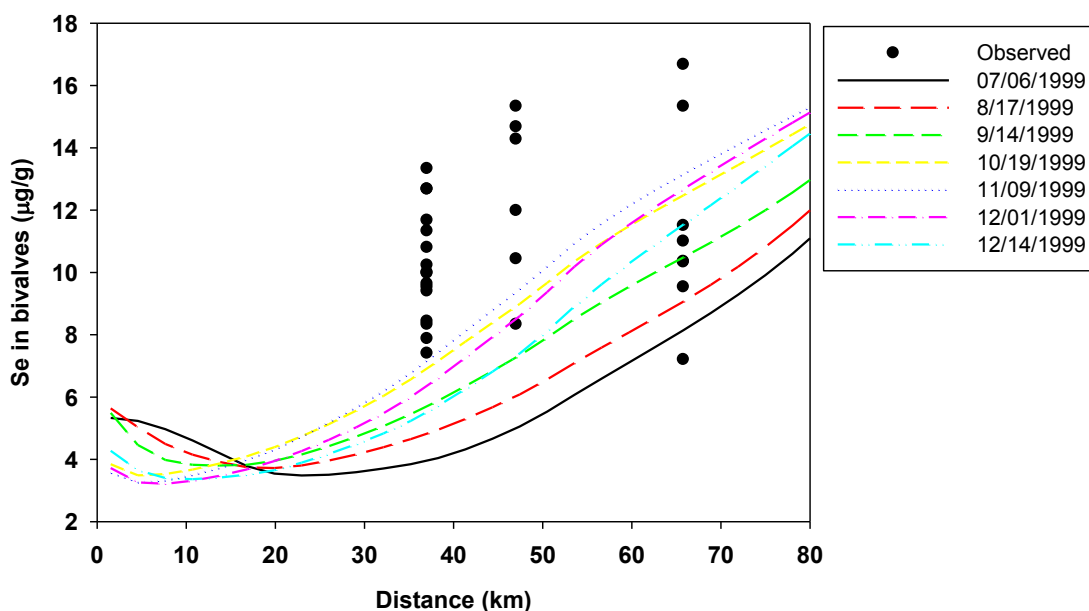


Figure 3-29 Simulated selenium concentrations in *Corbula amurensis* as a function of distance during sampling dates (using IR = 0.45, AE = 0.20 (for particulate elemental selenium), 0.45 (particulate adsorbed selenite and selenate) and 0.80 (particulate organic selenide)) compared to the observed values.

The model simulated Se:C ratio in phytoplankton was compared in Figure 3-30 to reported Se:C ratios for several species of phytoplankton, measured under selenite concentrations of 0.15 nM (0.0118 µg/L, concentrations found in NSFB) by Baines et al. (2001). The phytoplankton species *Prorocentrum minimum* is common in San Francisco Bay. Simulated Se:C ratios were also comparable to the mean observed value in the Delta plankton (Baines et al. 2004). This suggests that simulated selenium content in phytoplankton as tracked within the model is in the range of reported data.

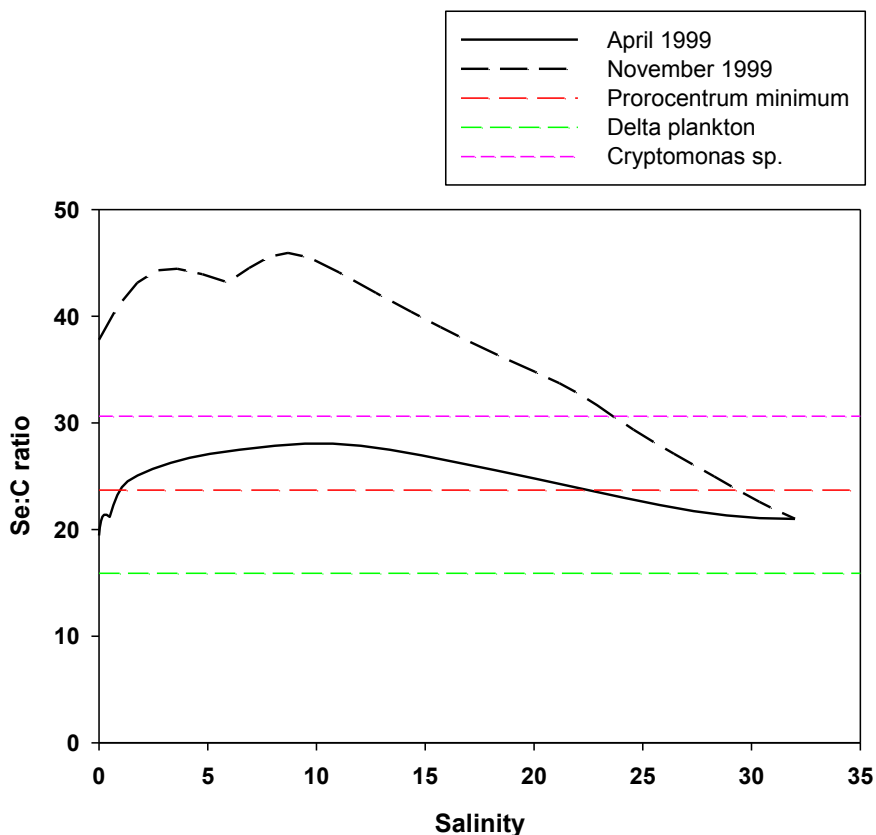


Figure 3-30 Model simulated Se:C ratio in phytoplankton for April and November 1999 compared to Se:C ratios in *Prorocentrum minimum*, and *Cryptomonas sp.* (measured under 0.15nM selenite by Baines and Fisher 2001) and Se:C ratio in Delta plankton. *P. minimum* and *Cryptomonas sp.* are common species in NSFB.

Simulated selenium concentrations in bottom sediments were also compared to observed values (Figure 3-31). Estimated selenium concentrations in bottom sediments are generally between 0.18- 0.22 $\mu\text{g/g}$, slightly lower than observed mean concentration of 0.25 $\mu\text{g/g}$. The simulated selenium concentrations in sediments show less variation than the observed values. The reason is partly due to the use of a 1-D representation of the sediment bed, and partly due to analytical variability in sediment data.

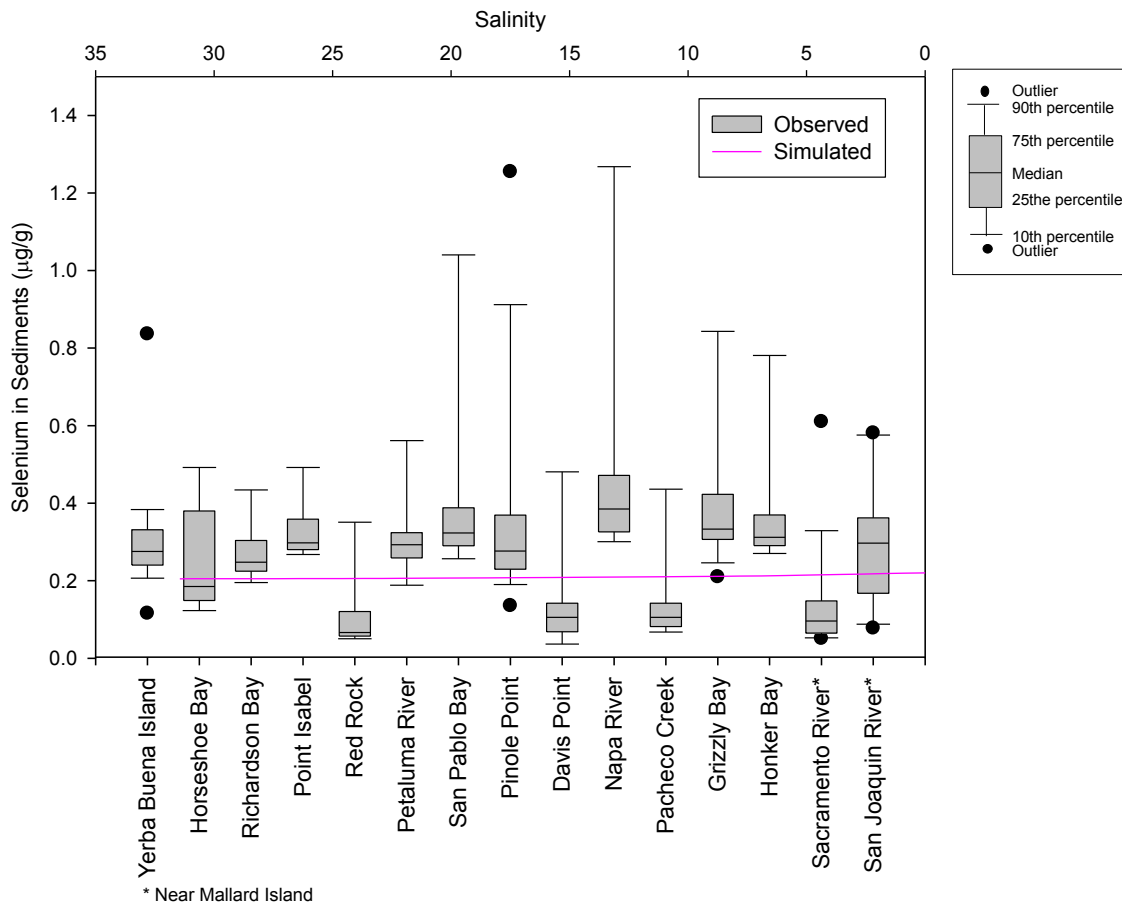


Figure 3-31 Model predicted selenium concentrations in bottom sediments (solid line) compared to observations at different locations, represented as a box plot.

Predicted estuarine-wide selenium concentrations in livers of surf scoter and sturgeon are $186.1 \pm 93.9 \mu\text{g/g}$ and $27.3 \pm 16.4 \mu\text{g/g}$ for November 1999. Predicted mean concentrations in livers of sturgeon compared well with the observed data of $24.1 \pm 10.3 \mu\text{g/g}$ (USGS, unpublished). The selenium concentrations in white sturgeon as presented in TM4 (Tetra Tech, 2008b) are data for 2000-2001 collected at Pittsburg Sturgeon Derby by USGS. White sturgeon sampled from San Francisco Bay-Delta between 1986 and 1990 contained selenium at concentrations ranging from 9 to $30 \mu\text{g/g dw}$ (mean: $26.55 \mu\text{g/g}$) in liver and 7 to $15 \mu\text{g/g}$ in muscle tissue (mean: $12.57 \mu\text{g/g}$; Urquhart and Regalado 1991; White et al. 1988). Lower selenium concentrations in livers of white sturgeon were reported by another study (mean: $9.75 \mu\text{g/g}$) between 2002 and 2004 (Linares et al. 2004, cited in Linville, 2006). Predicted selenium concentrations in muscle tissue of white sturgeon are $10.7 \mu\text{g/g}$ using a trophic transfer factor (TTF) of 1.7. Predicted selenium concentrations in white sturgeon liver and tissue over time compared to the observed data at different locations of the bay (e.g. Suisun Bay, San Pablo Bay, and Carquinez Strait) are shown in Figure 3-32 to Figure 3-34.

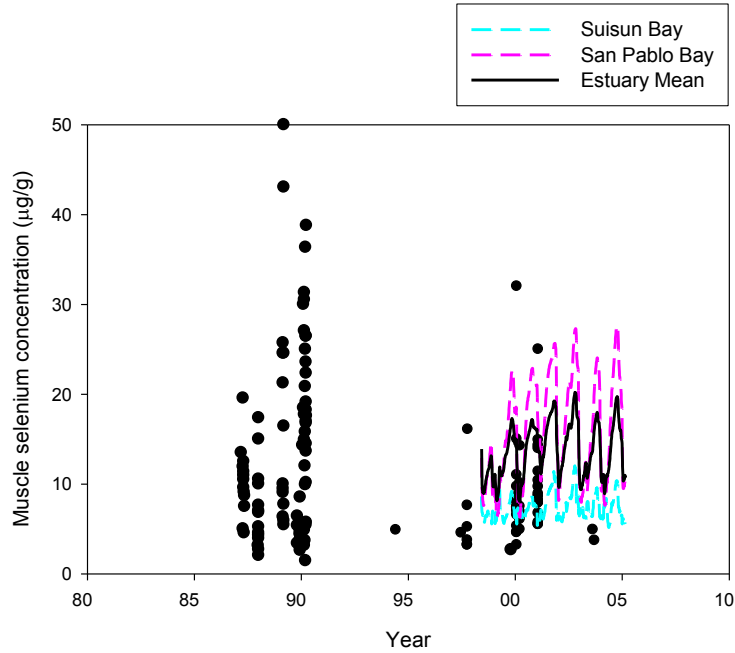


Figure 3-32 Model predicted selenium concentrations in muscle tissue of white sturgeon at Suisun Bay and San Pablo Bay compared to observed values (White et al., 1988, 1989, Urquhart et al., 1991, USGS and SFEI), using TTF = 1.7.

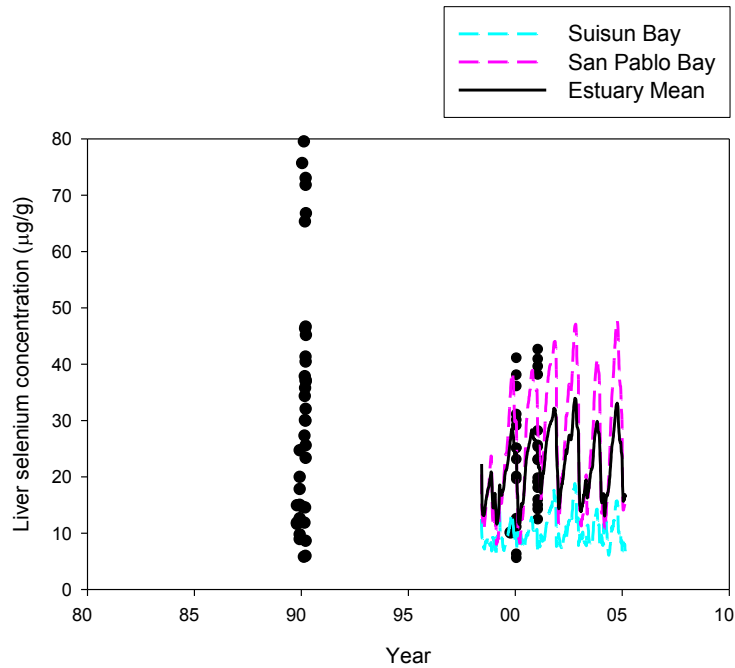


Figure 3-33 Model predicted selenium concentrations in liver of white sturgeon at Suisun Bay and San Pablo Bay compared to observed values (White et al., 1988, 1989, Urquhart et al., 1991, USGS and SFEI), using Eq. (27).

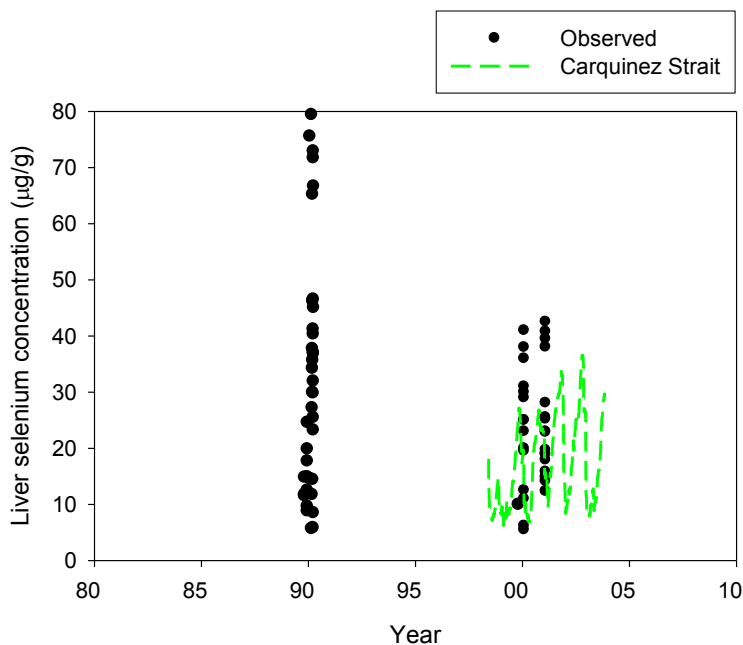


Figure 3-34 Model predicted selenium concentrations in liver tissue of white sturgeon at Carquinez strait compared to observed values (White et al., 1988, 1989, Urquhart et al., 1991, USGS and SFEI), using Eq. (27).

Selenium concentrations in muscle tissues of surf scoter and greater scaup are available for the recent years from SFEI (J.Hunt, personal communication). Relationships relating selenium concentrations in bivalves to selenium concentrations in muscle tissues of diving ducks however are only available for *Corbicula* (Presser and Luoma, 2006). With a TTF of 1.8 for scaup, predicted tissue selenium concentrations for scaup are 17.5 µg/g. The predicted concentrations are higher than the observed mean concentration of 12.6 µg/g (J.Hunt, personal communication) in Suisun Bay and San Pablo Bay. Predicted selenium concentrations in muscle tissue by location and time are compared to observed data (Figure 3-40).

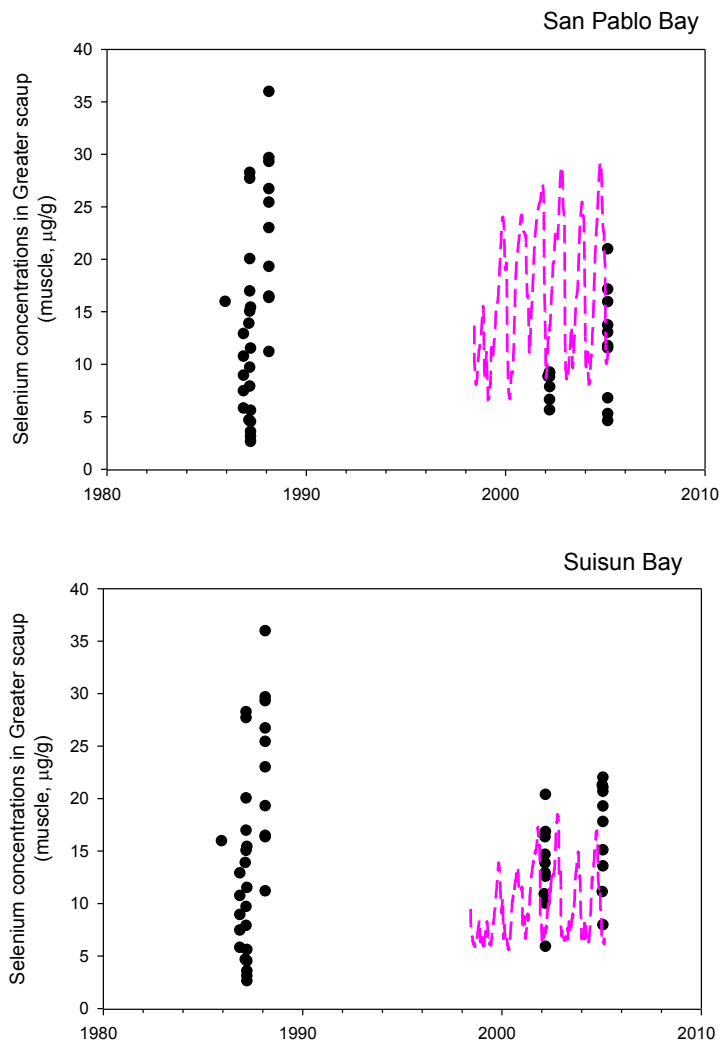


Figure 3-35 Model predicted selenium concentrations muscle tissue of diving ducks (dry weight; Greater Scaup) compared to observed data in San Pablo Bay and Suisun Bay, respectively (White et al., 1988, 1989; Urquhart et al., 1991; SFEI), using TTF = 1.8.

HQs for Lesser Scaup, Greater Scaup and Surf Scoter were estimated for three avian species assuming that nearly 100% of their diet consists of clams with concentrations predicted in Figure 3-29. The HQ values are shown in Figure 3-36 and range from less than 1 to about 3, indicating that there is some potential risk to these species at current concentrations. However, because of the conservative nature of the factors in the TRV calculation, the risks are considered to be relatively low.

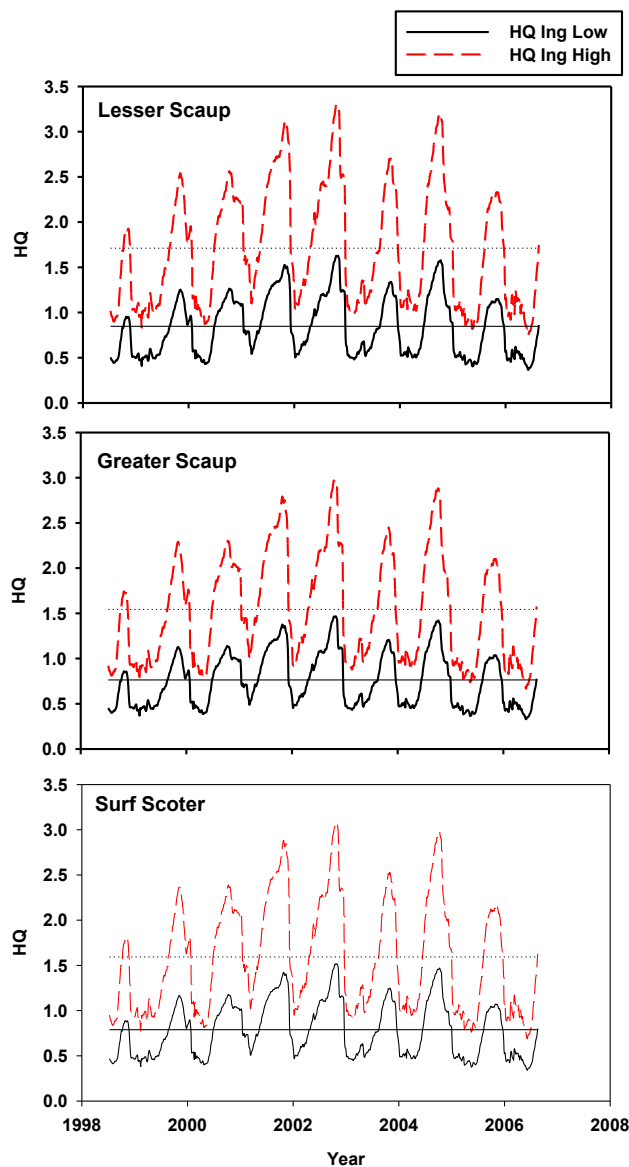


Figure 3-36 Model predicted hazard quotient for Lesser Scaup, Greater Scaup, and Surf Scoter for low and high ingestion TRVs (threshold reference value). Solid and dashed lines are predicted mean HQ values.

3.5. MODEL HINDCAST

A model hindcast is another form of evaluation and provides insight on model's capability to simulate conditions that are different from the calibration period in terms of hydrology and internal selenium loading. The calibrated model was run to hindcast selenium concentrations during two time periods prior to refinery clean-up, 1986 and 1998. To simulate selenium concentrations in 1986 and 1998, river discharges from the Sacramento River at Rio Vista and the San Joaquin River at Jersey Point for 1986 and 1998 were used (obtained from IEP). Selenium loads of different species from the refineries for 1986 and 1998 were data from Meseck (2002). Specifically, selenium loads from refineries for these two time periods are listed in Figure 3-6. To run the model for 1998, the simulations were

started on Oct. 1st, 1997. To run the model for 1986 the simulations were started on Oct. 1st, 1985.

Table 3-7
Selenium Loads from Refineries for 1986 and 1998 (after Meseck, 2002).

Refinery	Year	Selenite (kg/d)	Selenate (kg/d)	Organic Selenide (kg/d)	Total Selenium (kg/d)
Chevron	1986	0.66	0.20	0.11	0.98
Valero (Exxon)	1986	0.45	0.11	0.02	0.57
Shell	1986	1.59	0.30	0.08	2.00
Tesoro (Tosco)	1986	0.02	0.11	0.10	0.23
Conoco (Rodeo) Phillips	1986	0.82	0.27	0.11	1.21
Total					4.99
Chevron	1998	0.12	0.20	0.13	0.45
Shell	1998	0.28	0.47	0.32	1.07
Valero (Exxon)	1998	0.28	0.48	0.32	1.09
Tesoro (Tosco)	1998	0.06	0.08	0.06	0.20
Conoco Phillips (Rodeo)	1998	0.28	0.55	0.38	1.22
Total					4.02

Selenium loads from different sources (riverine, refineries, and tributaries) used for the model simulation years (1986, 1998 and 1999 forward) are shown in Figure 3-37. Selenium loads from the rivers show large variation. Water year 1998 shows the highest riverine selenium loads due to high inflows. Selenium loads from refineries show marked decrease from 1998 to 1999. Current selenium loads from refineries are around one-third of the previous loads (prior to refinery clean-up).

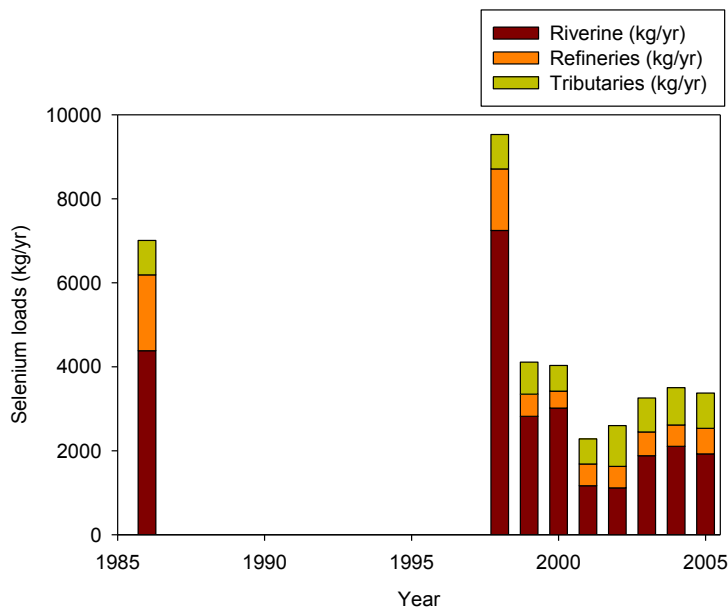


Figure 3-37 Annual selenium loads from riverine (Sacramento River + San Joaquin), refineries and local tributaries for prior to refinery clean-up (1986 and 1998) and post refinery clean-up (1999-2005) used in the model. Refinery loads for 1986 and 1998 are from Meseck (2002).

Figure 3-38 to Figure 3-43 show the model hindcast results for 1998. For June (high flow) and October 1998 (low flow), the model-simulated salinity compared well with the observed values. Simulated TSM for October 1998 is able to capture the ETM. Phytoplankton concentrations are simulated well for June 1998 but are over-predicted in October 1998. Model hindcast results for dissolved selenium species for both low and high flow show very good results. The model is able to simulate the relatively conservative mixing behavior of selenite, selenate and organic selenide during high flow (Figure 3-38). For a low flow month (October 1998), it is worth noting that the mid-estuarine peaks in selenite and selenate are simulated well by the model. This indicates that the spatial distribution of selenium inputs from local sources and the transport of dissolved selenium species have been well represented. Spatial patterns in selenite and organic selenide were also captured well by the model (Figure 3-39).

Simulated particulate selenium concentrations compared well with the observed values (Figure 3-40; GOFs = -16.7% to 84.1%). Total dissolved and particulate selenium for June and October 1998 were simulated well by the model (Figure 3-41). Simulated selenium content on particulates for June and October 1998 are very close to the observed values (Figure 3-42). Particularly for the low flow month in October 1998, spatial patterns in particulate selenium were captured well by the model. In some cases, higher particulate elemental selenium and particulate organic selenium concentrations were observed than the simulations. This may be due to in-situ processes of sediment resuspension, which result in higher particulate elemental selenium or variations in phytoplankton concentrations or species that may result in higher particulate organic selenium. These processes are not captured by the model and may explain the differences between observations and simulations in these plots.

The model hindcast for 1986 indicates salinity, TSM and chlorophyll a concentrations are simulated correctly by the model without additional calibration (Figure 3-43). For dissolved selenium, the relatively conservative mixing behavior during high flow (April 1986) and the mid-estuarine peaks during low flow (September 1986) for selenite and selenate are captured well by the model (Figure 3-44). Model-simulated total dissolved and particulate selenium concentrations compared to the observed data are shown in Figure 3-45.

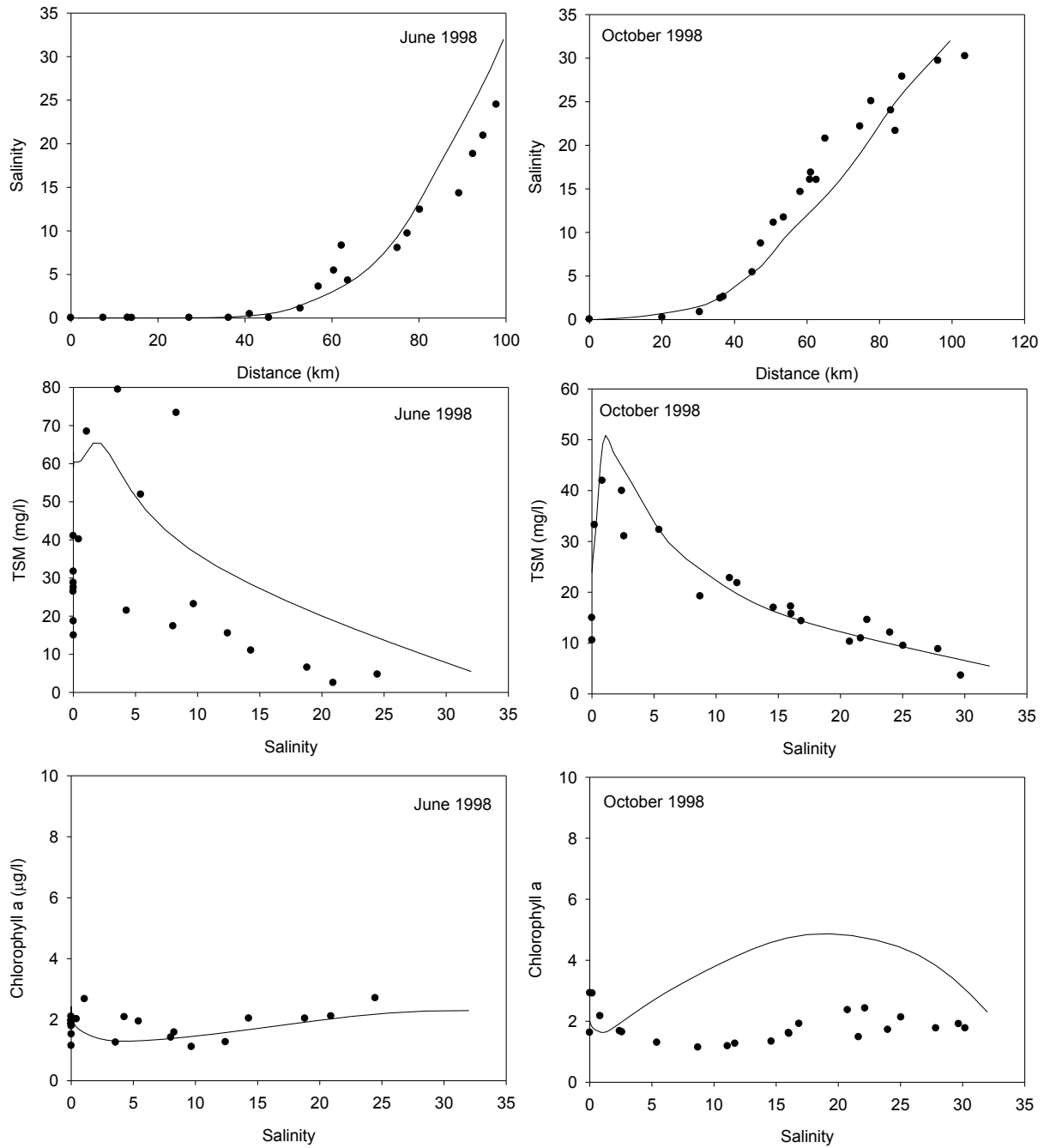


Figure 3-38 Model simulated profiles of salinity, TSM and chlorophyll a compared to observed values for June and October 1998.

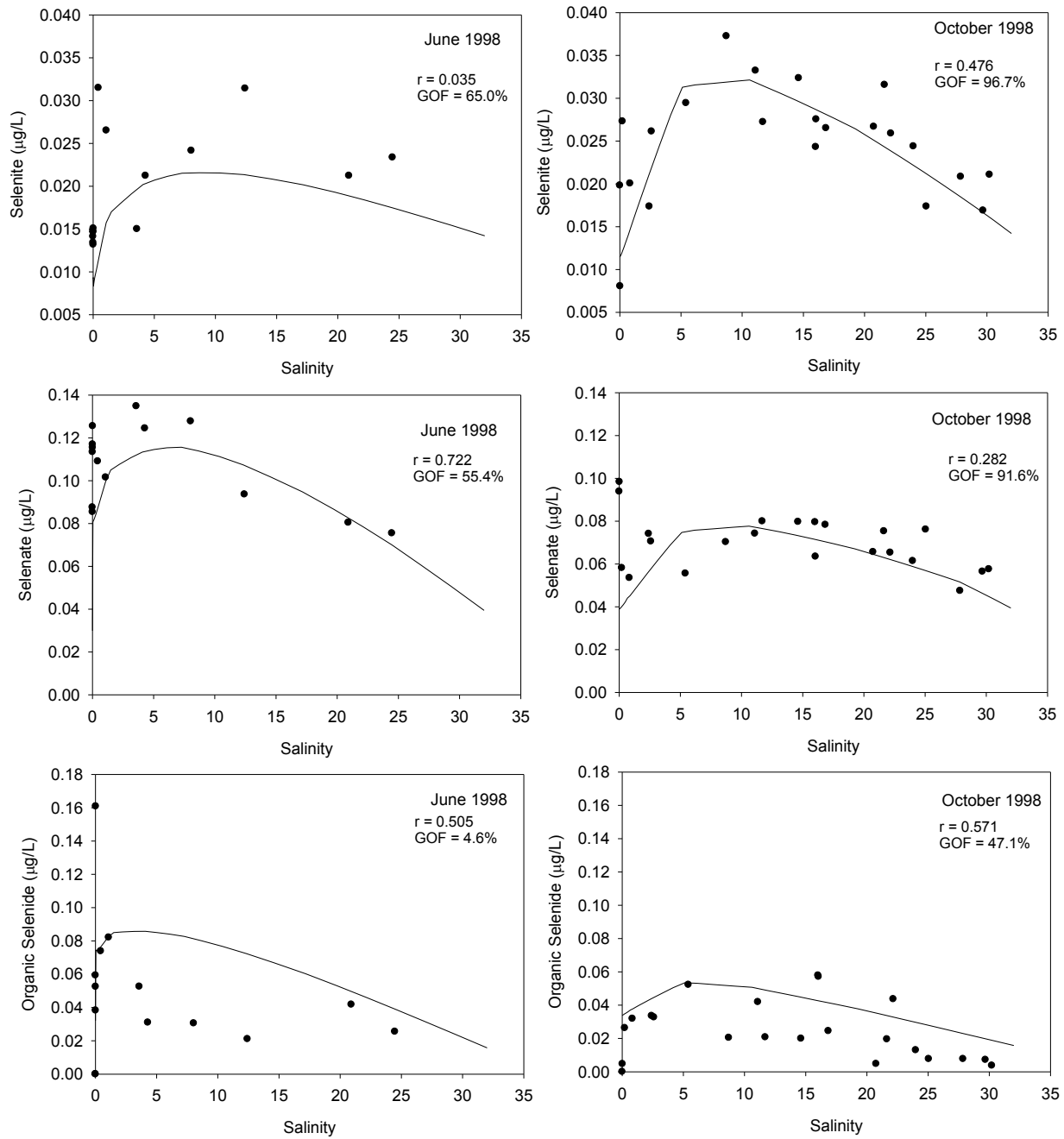


Figure 3-39 Model simulated dissolved selenium by species as a function of salinity compared to observed values for June 1998 and October 1998.

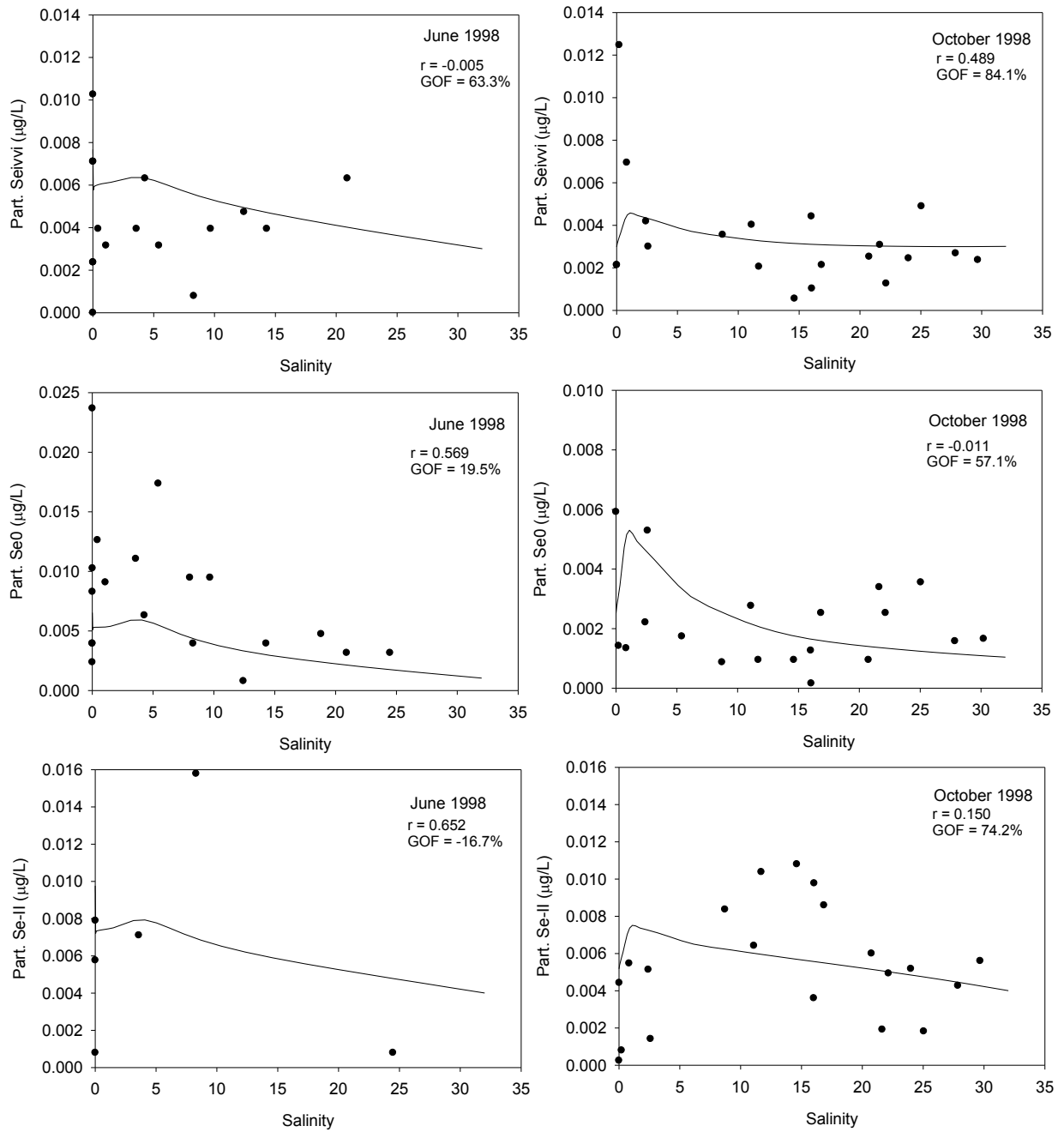


Figure 3-40 Model simulated particulate selenium by species compared to observed values for June 1998 and October 1998.

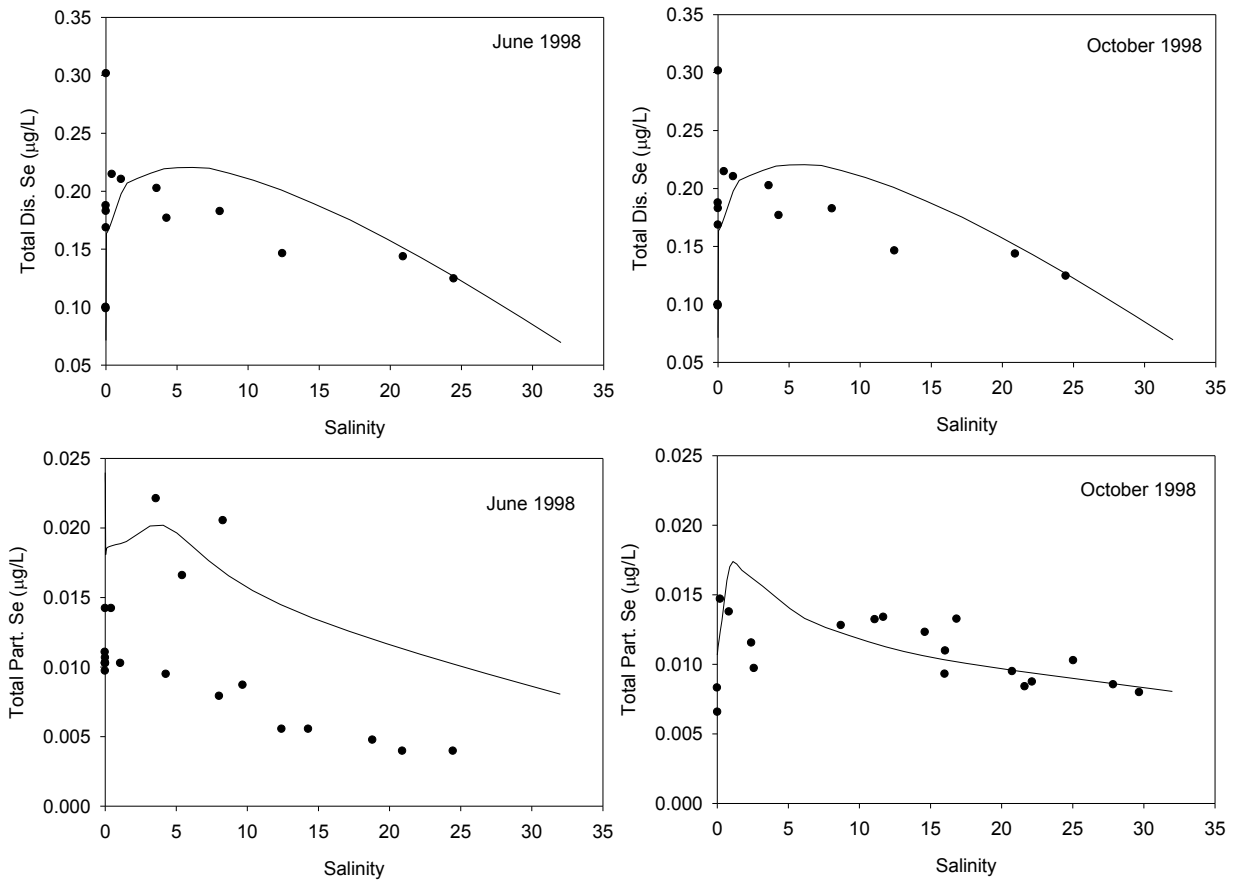


Figure 3-41 Model simulated total dissolved and particulate selenium compared to observed values for June 1998 and October 1998.

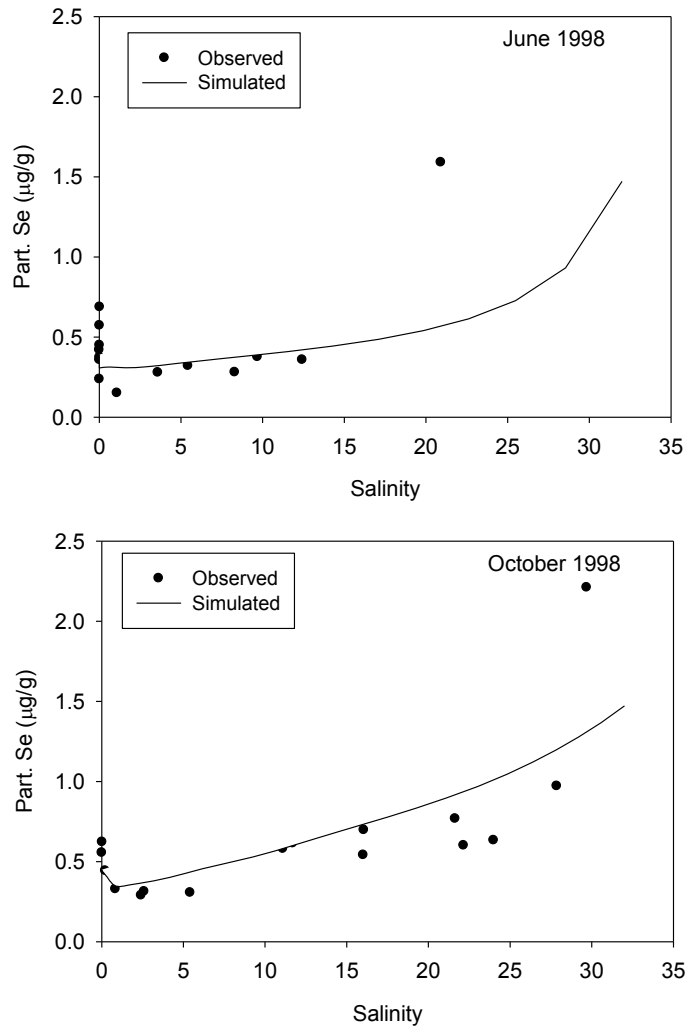


Figure 3-42 Model evaluation of simulated particulate selenium for high flow (June 1998) and low flow (October 1998) in 1998.

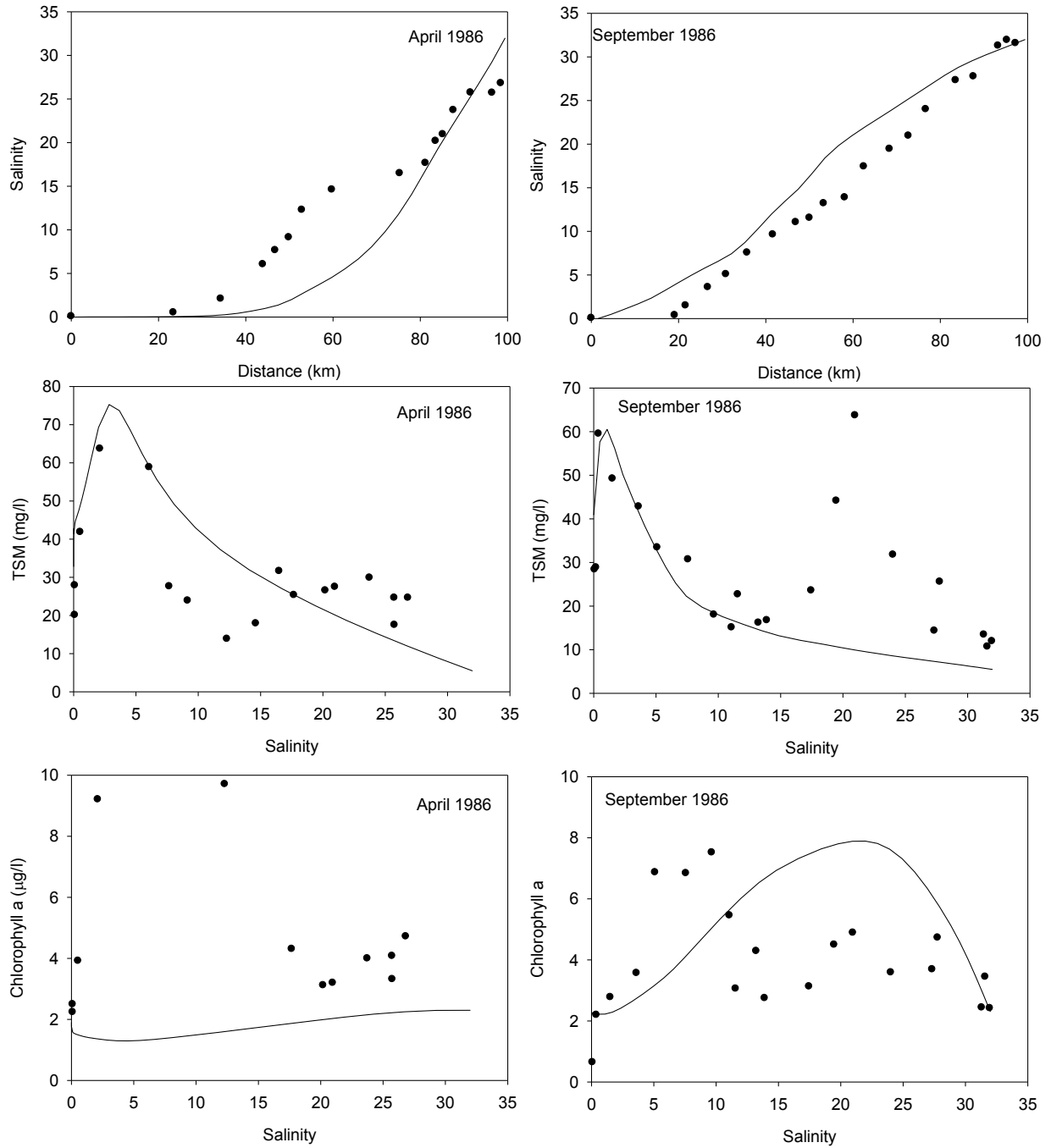


Figure 3-43 Model simulated profiles of salinity, TSM and chlorophyll a compared to observed values for April and September 1986.

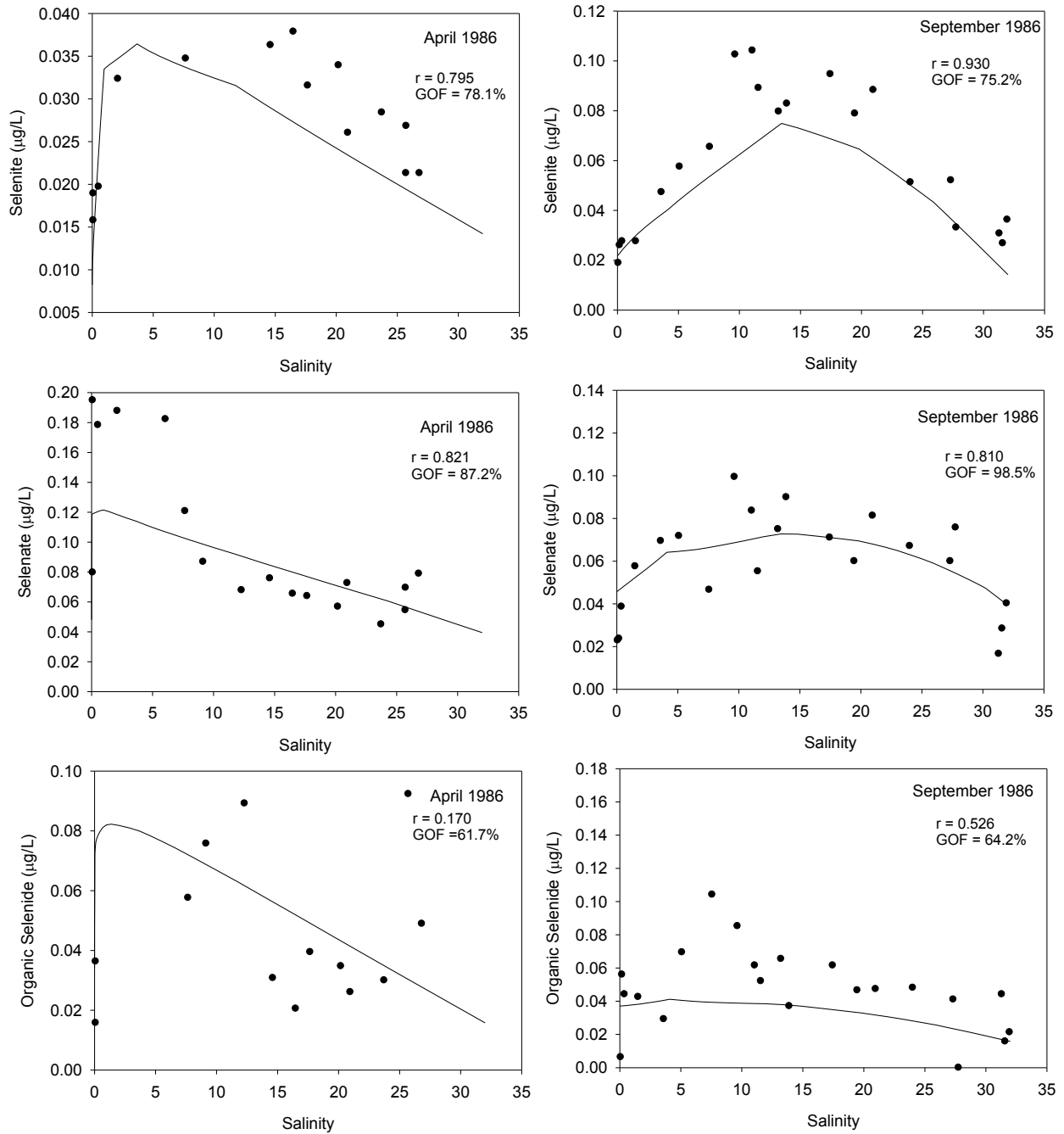


Figure 3-44 Model simulated dissolved selenium by species compared to the observed values for April 1986 and October 1986.

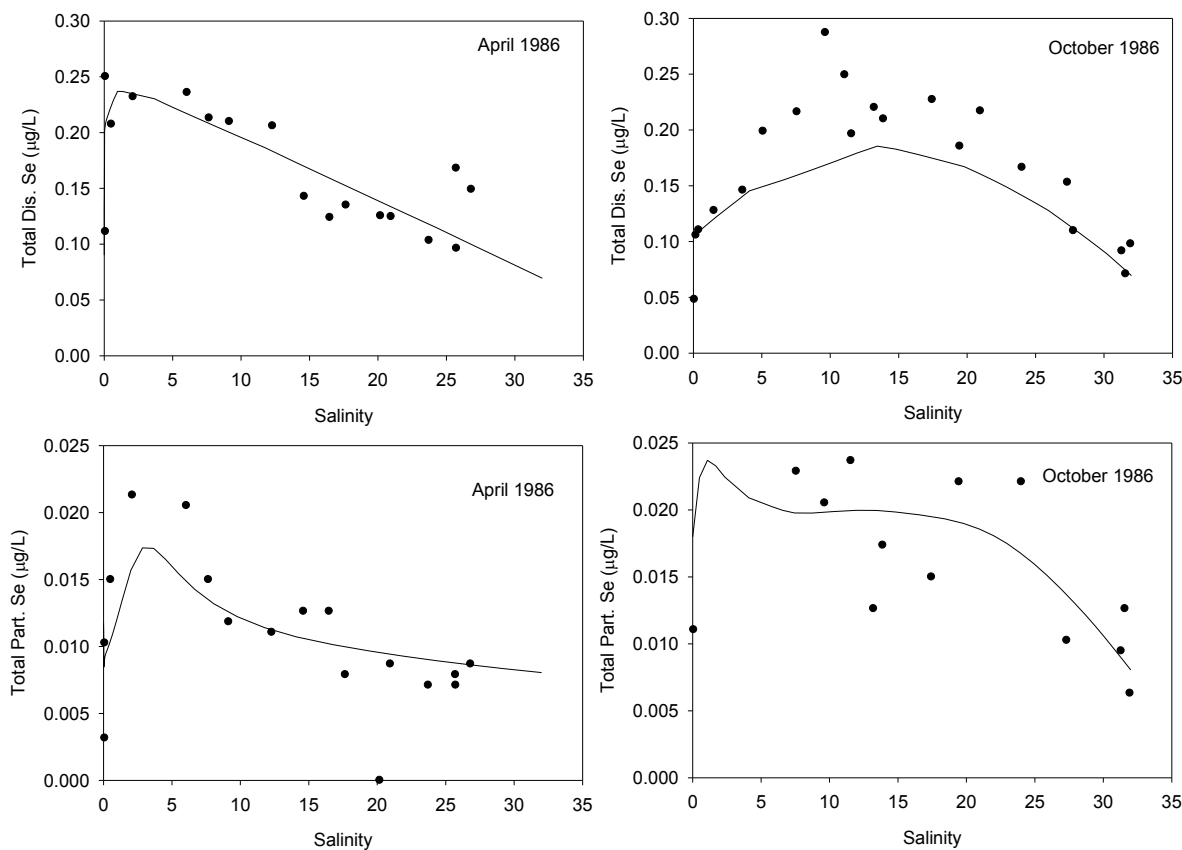


Figure 3-45 Model simulated total dissolved and particulate selenium compared to the observed values for April and October 1986.

3.6. SUMMARY OF MODEL CALIBRATION AND EVALUATION

The extensive database on physical and biological constituents, was complemented with the more limited selenium speciation data, to calibrate the ECoS-NSFB model. In general, salinity was calibrated with greatest precision for all dates. Calibrated fits were poorer for other constituents such as suspended sediments and phytoplankton, likely related to the complexity of factors that influence those constituents. Selenium fits were reasonable, although not as good as salinity. Organic selenium fits were relatively poor, and the large variation in observed data could not be captured by varying the uptake and mineralization rates of organic selenium. This is possibly caused by measurement error in the observed data, or by sources/transformations that have not adequately represented in the model. For all parameters modeled, the model is better able to represent average conditions than spatial and temporal peaks in concentration.

The calibrated model was evaluated against data from other periods. It was found that day-to-day evaluations were not as good as the longer term evaluations for constituents such as phytoplankton and TSM for which such data exist. The selenium values were compared against RMP measurements, and the fits were surprisingly good given the differing source and collection methods of that data set. Model hindcasts, where the currently calibrated model was compared against selenium values from the mid-1980s, were also very good, despite the changes in the source magnitude/speciation and hydrology.

In summary, this effort has demonstrated the ability of the ECoS-based model to represent key features of relevance to selenium fate and transport. In the following section, the calibrated model is tested further under different conditions to better understand its performance, and by extension, the behavior of selenium in NSFB.

4. EXPANDED TESTING AND EXPLORATION OF MODEL PERFORMANCE

Following calibration and evaluation against new data, a series of model runs were conducted to gain more confidence and insight in the model's performance. The goal of the effort was to run the model under different input conditions and with different parameter values to assess the impact to selenium species concentrations. These tests provide insight into the functioning of the model, by identifying processes and variables that are especially sensitive to inputs, or by assessing whether the key variables of interest in this work, e.g., selenium in particulates, are sensitive to other less well-modeled constituents. Another objective of these tests was to evaluate the effect on selenium of parameters where the model fit is not very good, such as phytoplankton. The runs were also used to present summary information, such as mass balances that may be used as a high-level check of the model performance. The runs/testing performed fall into the following seven categories:

- Sensitivity analyses: The calibrated model parameters are perturbed from their base case values to assess whether specific dependent variables respond significantly. Future model development and/or data collection must be targeted at the most sensitive parameters.
- Changing chlorophyll a: The model calibration and evaluation shows that chlorophyll a concentrations were sometimes fit poorly using the ECoS-NSFB framework. The reasons for the poor fit are explored in Section 3, and these additional testing was reported to understand the importance of chlorophyll a variation to the predicted values of particulate selenium.
- Changing uptake rates of dissolved selenium species: The uptake rates for selenate, selenite, and dissolved organic selenide are based on literature reports and calibrated to fit the data. Testing was performed to explore the impact of varying the rates over a wide range, from 10 to 100 times the rates in the base case calibration.
- Different boundary conditions for riverine and seawater input: Particulate selenium concentrations in the riverine and seawater boundary have a significant impact on the concentrations in the bay, and are defined by a small amount of data. A range of values for both boundary conditions was used to evaluate simulated values in the bay.
- Relative contribution of different sources of particulate selenium: Because particulate selenium concentrations are the single most important constituent with respect to bivalve uptake, a more detailed evaluation of the sources (riverine, in-Bay sediment erosion, or phytoplankton) and estuary concentrations is presented.
- Spatial trends in particulate selenium: The model estimates an increase of particulate selenium (in μg) with distance across the estuary. The observed data are explored more fully to evaluate the model results of this key constituent for relating to biological uptake.
- Mass balance of selenium: In any modeling effort, a mass balance of inputs and outputs provides a check on the overall numerical representation. Selenium sources, outflows, and changes in stored mass in the water column are presented.

4.1. SENSITIVITY ANALYSIS

A sensitivity analysis was conducted previously by Meseck (2002) for a set of parameters and for various dissolved and particulate selenium concentrations. Under high flow, dissolved selenium concentrations were found to be most sensitive to the riverine inputs. The particulate selenium concentrations were sensitive to parameters that determine riverine inputs of TSM (a, b, c in equation 24), location of estuarine turbidity maximum, photosynthesis rate, and riverine discharge. Under low flow, particulate selenium was generally sensitive to the same set of parameters. In addition, particulate organic selenide was sensitive to selenium uptake rates by phytoplankton, phytoplankton growth rates and selenite oxidation rate.

The sensitivity analysis conducted in this new application of the ECoS framework was for a similar set of selected parameters that affect dissolved and particulate selenium concentrations in the water column. These parameters can be categorized as the Sacramento River and San Joaquin River load inputs (SeVI, SeIV, OrgSe in the Sacramento River and delta removal constants in the San Joaquin Rivers), selenium content on riverine particulates (PSe0, PSeII, and PSeivvi), phytoplankton uptake rates and growth rates (for SeVI, SeIV, SeII), selenite adsorption rate and parameters that determine locations of estuarine turbidity maximum (d in equation 4) and some selenium transformation rates (PSeII mineralization rate k1, partition coefficient for selenite kd). The sensitivity was mainly conducted for a low flow date, November 11 1999. The sensitivity analysis was conducted by altering the parameters for $\pm 50\%$ and estimating the relative changes in resulted selenium concentrations. The sensitivity is defined as the ratio between the relative changes in resulted parameters to the relative changes in the inputs ($S_{c,k}$) as follows:

$$S_{c,k} = (1 - Cr/Cs)/(1-Kr/Ks) \quad (36)$$

where Cr = reference concentrations, Cs = simulation result when Kr is changed

Kr = reference parameter value, Ks is the adjusted parameter value. The variation of $\pm 50\%$ is approximately the same magnitude of variation as observed in particulate selenium content on riverine particulates and delta selenium load removal constant. When calculating the value of $S_{c,k}$ for each parameter, the model-predicted mean concentrations reference and adjusted parameter conditions were used. Thus, an average value of Cr (across the estuary from Rio Vista to Golden Gate) was computed for the reference case, and the average value of Cs was computed with the adjusted value of the selected parameter. These were used to calculate $S_{c,k}$. Note the value of the numerator in equation (36) can take one of two values for the $\pm 50\%$ change in parameter values (-1 or 0.33).

The results indicate that dissolved and particulate selenium concentrations are most sensitive to riverine input parameters (Table 4-1). Particulate selenium concentrations are sensitive to selenium content on particulate material at the head of the estuary. Dissolved and particulate selenium are less sensitive to selenium transformation coefficients such as phytoplankton uptake and selenite adsorption rates. The model is relatively sensitive to parameters that affect the location and magnitude of the TSM. Particulate organic selenide and particulate selenium are also sensitive to increases in phytoplankton growth rates. The relatively high sensitivity of particulate organic selenium, dissolved selenite and particulate selenium to

increases in phytoplankton growth rate (also as an indicator of phytoplankton concentrations) indicates that certain species of selenium are closely tied to phytoplankton concentrations. In addition, particulate organic selenide is also sensitive to its mineralization rate (k_1).

Figure 4-1 shows the sensitivity of dissolved selenium (selenate, selenite and organic selenide) to changes in riverine input. Overall, dissolved selenium is very sensitive to changes in riverine inputs. The effects are most significant at the head of the estuary, and due to mixing with seawater, which is defined by boundary conditions for various constituents such as salinity, selenium, phytoplankton, etc., the effects become smaller with transport distance along the estuary. Particulate selenium (adsorbed selenite and selenate, particulate organic selenide, and particulate elemental selenium, expressed as $\mu\text{g/L}$) is also sensitive to changes in riverine inputs (Figure 4-2). Sensitivity of particulate organic selenide concentrations to phytoplankton growth rate, mineralization rate, selenium content in phytoplankton in the riverine and seawater endmembers, scaling factors of U_{beps} and K_{beps} are shown in Figure 4-3 to 4-4.

Model simulated particulate selenium concentration (in $\mu\text{g/g}$) is sensitive to parameter used in specifying riverine TSM concentration as a function of flow (Figure 4-5a). In simulating particulate selenium concentrations, selenium concentration in phytoplankton in seawater and riverine end members are important parameters. Particulate selenium concentrations are relatively sensitive to seawater endmember phytoplankton selenium concentration and not very sensitive to riverine phytoplankton selenium (Figure 4-5b, c).

Table 4-1
Sensitivity Analysis for Changing Parameters by 50% During Low Flow (Nov. 1999).
|Sc,k| < 0.15 is Insensitive.

	Org.Se	SeVI	SeIV	P Org Se	P Seivvi	PSe0	Part. Se (ug/g)
SeVI SacRiv (+50%)		0.418	0.006	0.024	0.004		0.010
SeVI SacRiv (-50%)		0.195	-0.002	0.008	-0.001		0.003
SeIV SacRiv (+50%)			0.244	0.021	0.002		0.009
SeIV SacRiv (-50%)			0.097	0.007	0.001		0.003
OrgSe SacRiv (+50%)	0.399		0.084	0.029			0.012
OrgSe SacRiv (-50%)	0.181		0.030	0.010			0.004
SeVI SJR input (+50%) (Delta Removal Constant)		0.020		0.001			0.001
SeVI SJR input (-50%) (Delta Removal Constant)		0.007					
SeIV SJR input (+50%) (Delta Removal Constant)			0.000				
SeIV SJR input (-50%) (Delta Removal Constant)			0.001				
Sell SJR input (+50%) (Delta Removal Constant)	0.034		0.007	0.003			0.001
Sell SJR input (-50%) (Delta Removal Constant)	0.012		0.002	0.001			
Riverine PSe0 (+50%)						0.269	0.044
Riverine PSe0 (-50%)						0.109	0.015
Riverine PSell (+50%)	-0.004		-0.001	0.214			0.081
Riverine PSell (-50%)	0.002			0.061			0.019
Riverine Pseivvi (+50%)					0.304		0.071
Riverine Pseivvi (-50%)					0.127		0.025
Refinery SeIV (-50%)			0.026	0.010			0.004
Refinery SeIV (+50%)			0.073	0.003			0.001
SeVI uptake rate (+50%)	0.002	-0.006	-0.006	0.063			0.029
SeVI uptake rate (-50%)	0.001	-0.002	-0.002	0.022			0.010
SeIV uptake rate (+50%)	0.003		-0.029	0.089			0.042
SeIV uptake rate (-50%)	0.001		-0.010	0.032			0.015
Sell uptake rate (+50%)	-0.011		-0.002	0.058			0.027
Sell uptake rate (-50%)	-0.004		-0.001	0.020			0.009
Selenite adsorption rate (+50%)							
Selenite adsorption rate (-50%)					0.001		
Phytoplankton growth rate (+50%)	0.047	0.062	0.245	-0.617			-0.295
Phytoplankton growth rate (-50%)	-0.002	-0.002	-0.011	0.085	-0.015		0.023
PSell mineralization rate k1 (+50%)	0.030			-0.161			-0.070
PSell mineralization rate k1 (-50%)	0.012			-0.055			-0.025
Partition coefficient kd (+50%)	-0.004	-0.002	0.005		0.006		0.001
Partition coefficient kd (-50%)	0.001	0.001	-0.002		0.002		0.001
Adsorption rate a (+50%)	-0.004	-0.002	0.005		0.008		0.001
Adsorption rate a (-50%)	0.001	0.001	-0.002		-0.001		0.000
Sacramento River Discharge (+50%)	-0.026	-0.039	-0.244	0.032	0.323		-0.269
Sacramento River Discharge (-50%)	-0.030	-0.018	-0.050	-0.331	0.120		-0.241
Phytoplankton Se in seawater (+50%)	0.012		0.001	0.395			0.297
Phytoplankton Se in seawater (-50%)	0.004		0.000	0.179			0.123
Riverine phytoplankton Se (+ 50%)	0.054	0.040	0.032	0.039	0.187	0.031	0.018
Riverine phytoplankton Se (-50%)	-0.018	-0.007	-0.011	-0.012	0.047	-0.010	-0.006
Scaling factor for Ubeps (+50%)	-0.001		0.012	0.645	0.706	1.539	-0.162
Scaling factor for Ubeps (-50%)	0.003	0.002	0.003	0.071	0.112	0.558	-0.101
Scaling factor for Kbeps (+50%)	-0.008	-0.006	-0.011	-0.180	-0.318	-1.543	0.305
Scaling factor for Kbeps (-50%)	-0.001		-0.005	-0.408	-0.437	-0.725	0.084
c (factor relates freshwater discharge and sediment input +50%)	0.372	0.011	0.113	3.033	3.783	4.157	-2.559
c (factor relates freshwater discharge and sediment input - 50%)	0.036	0.070	0.302	-0.962	1.451	2.865	-1.135
Dispersion coefficient (Kw) (+50%)	-0.148	-0.181	-0.108	0.080	0.134	0.418	0.023
Dispersion coefficient (Kw) (-50%)	-0.074	-0.086	-0.059	0.038	0.036	0.196	0.067

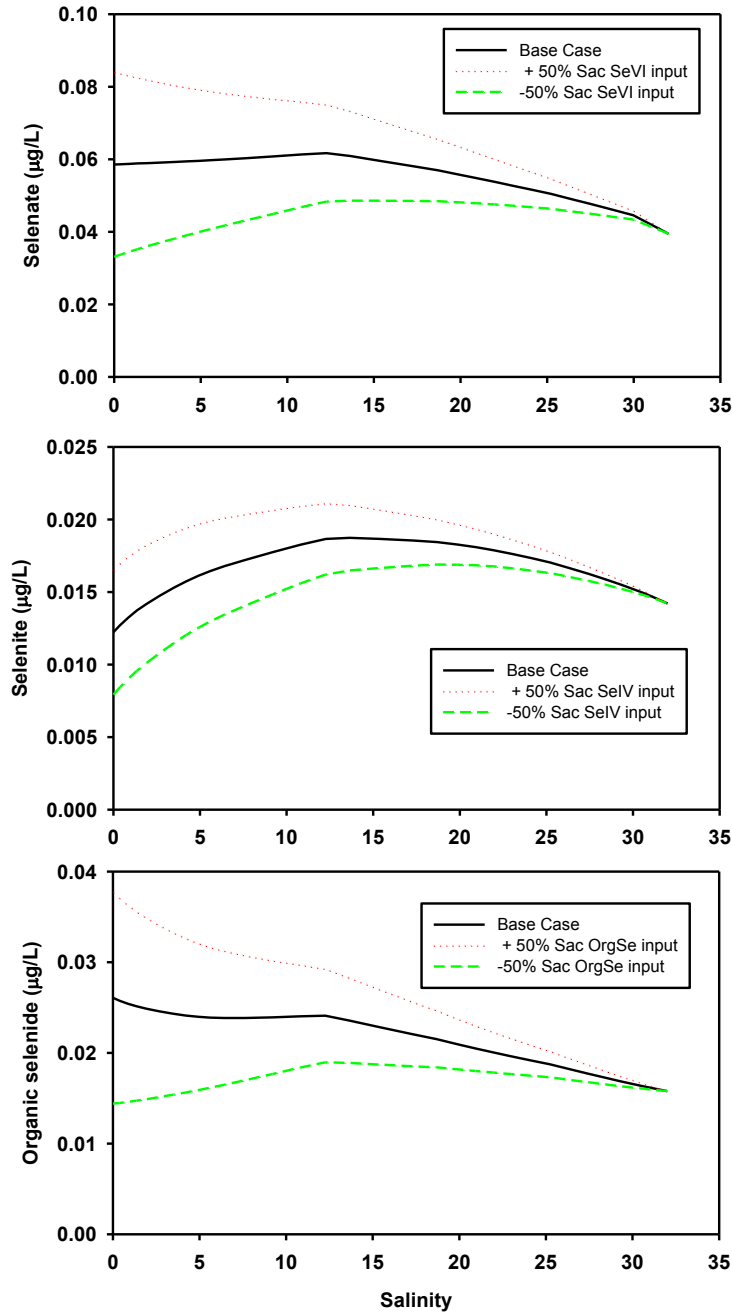


Figure 4-1 Model sensitivity of dissolved selenate, selenite and organic selenide concentrations during low flow to riverine inputs. Note the convergence of the plots at the seawater boundary in this and subsequent plots. This is a reflection of the boundary condition used in the model.

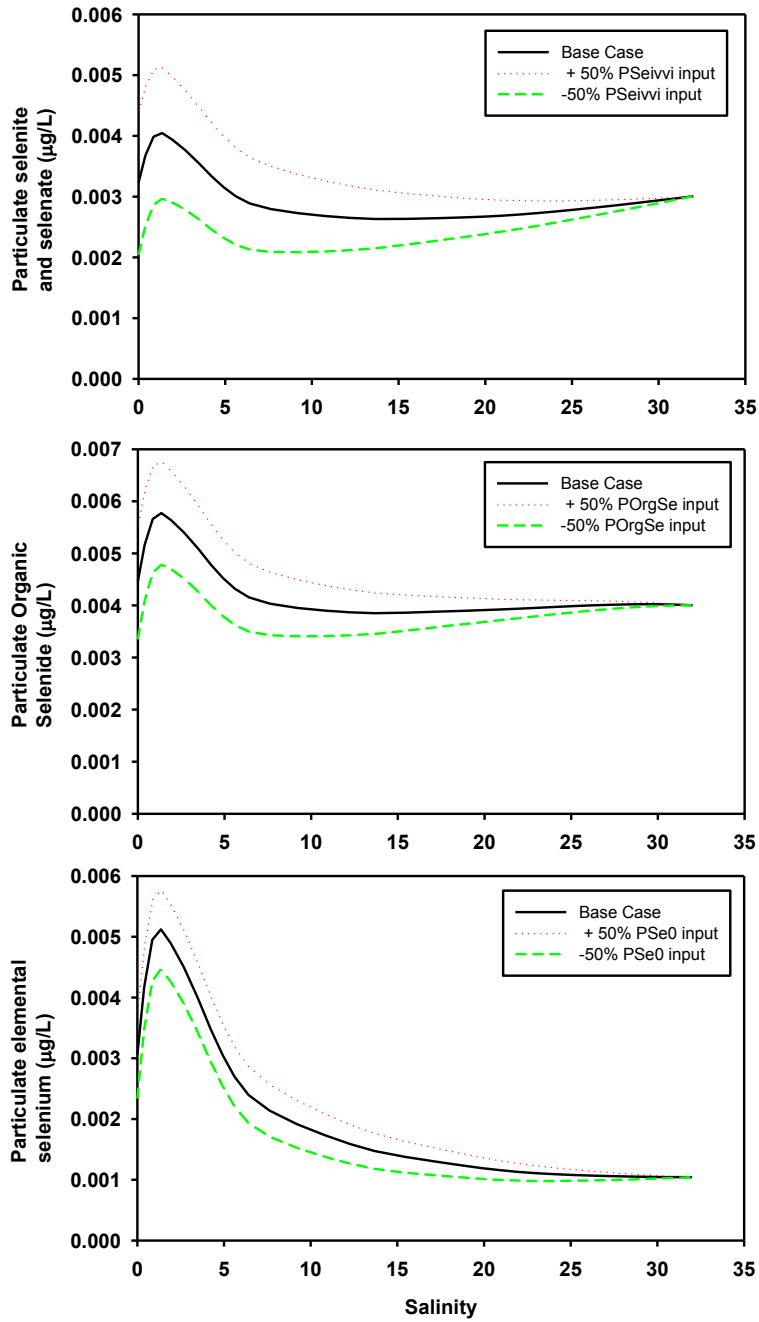


Figure 4-2 Model sensitivity of particulate adsorbed selenite + selenate, particulate organic selenide and particulate elemental selenium during low flow in response to changes in riverine inputs

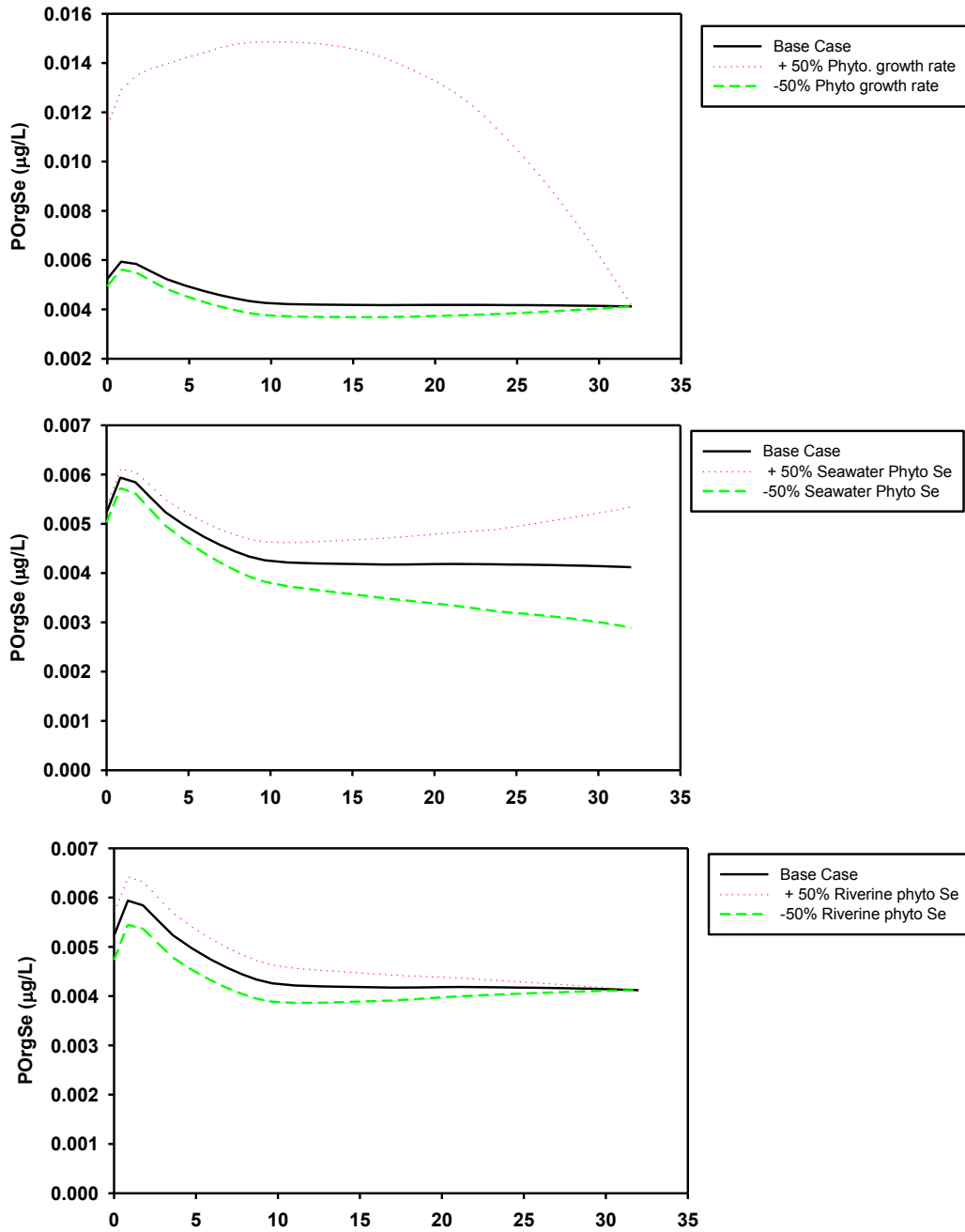


Figure 4-3 Modeled sensitivity of particulate organic selenide in low flow to changes in: a) phytoplankton growth rate, b) seawater phytoplankton selenium, and c) riverine phytoplankton selenium.

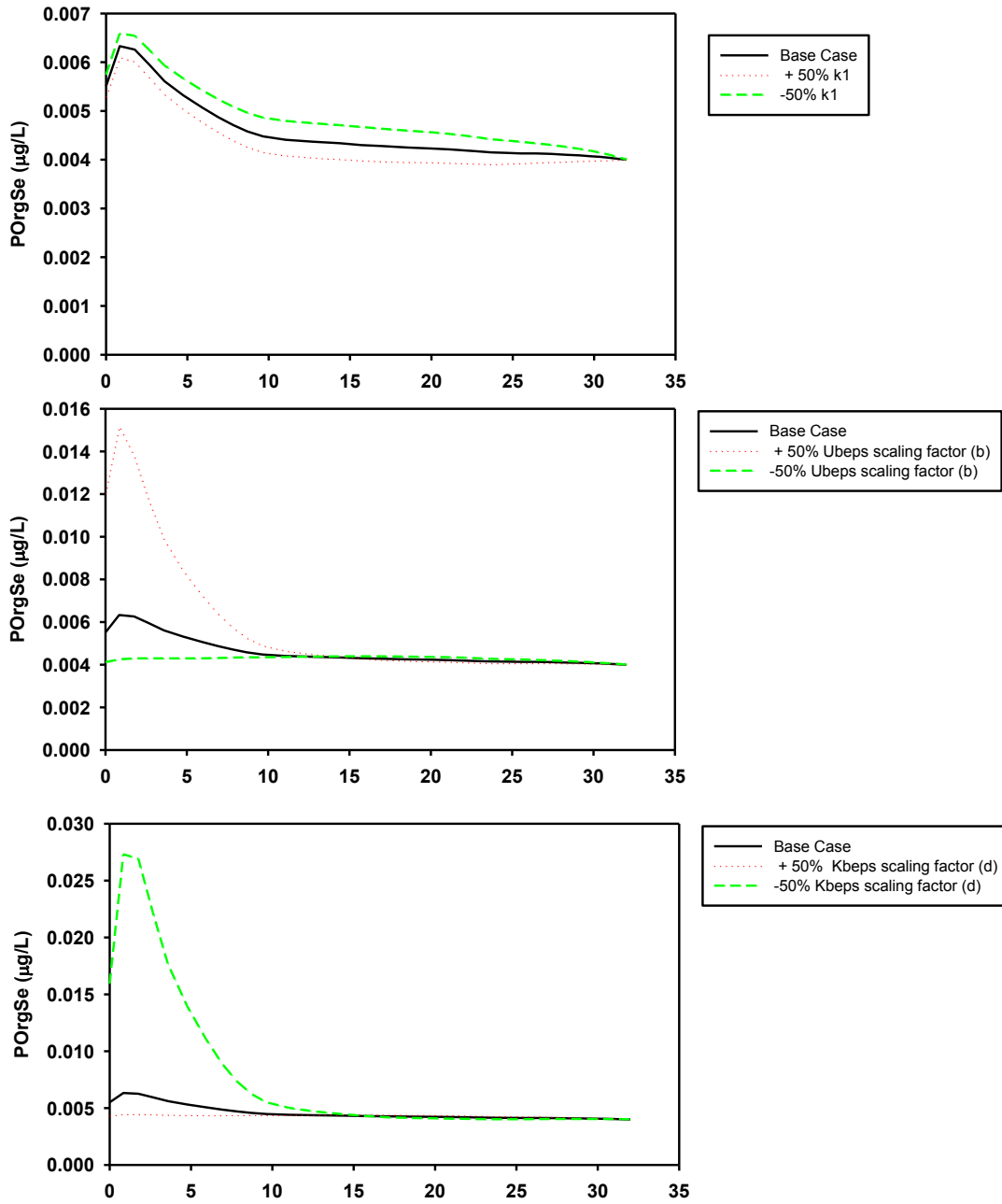


Figure 4-4 Modeled sensitivity of particulate organic selenide in low flow to changes in: a) mineralization rate k_1 , b) scaling factor in Ubepts (b), and c) scaling factor in Kbepts (d).

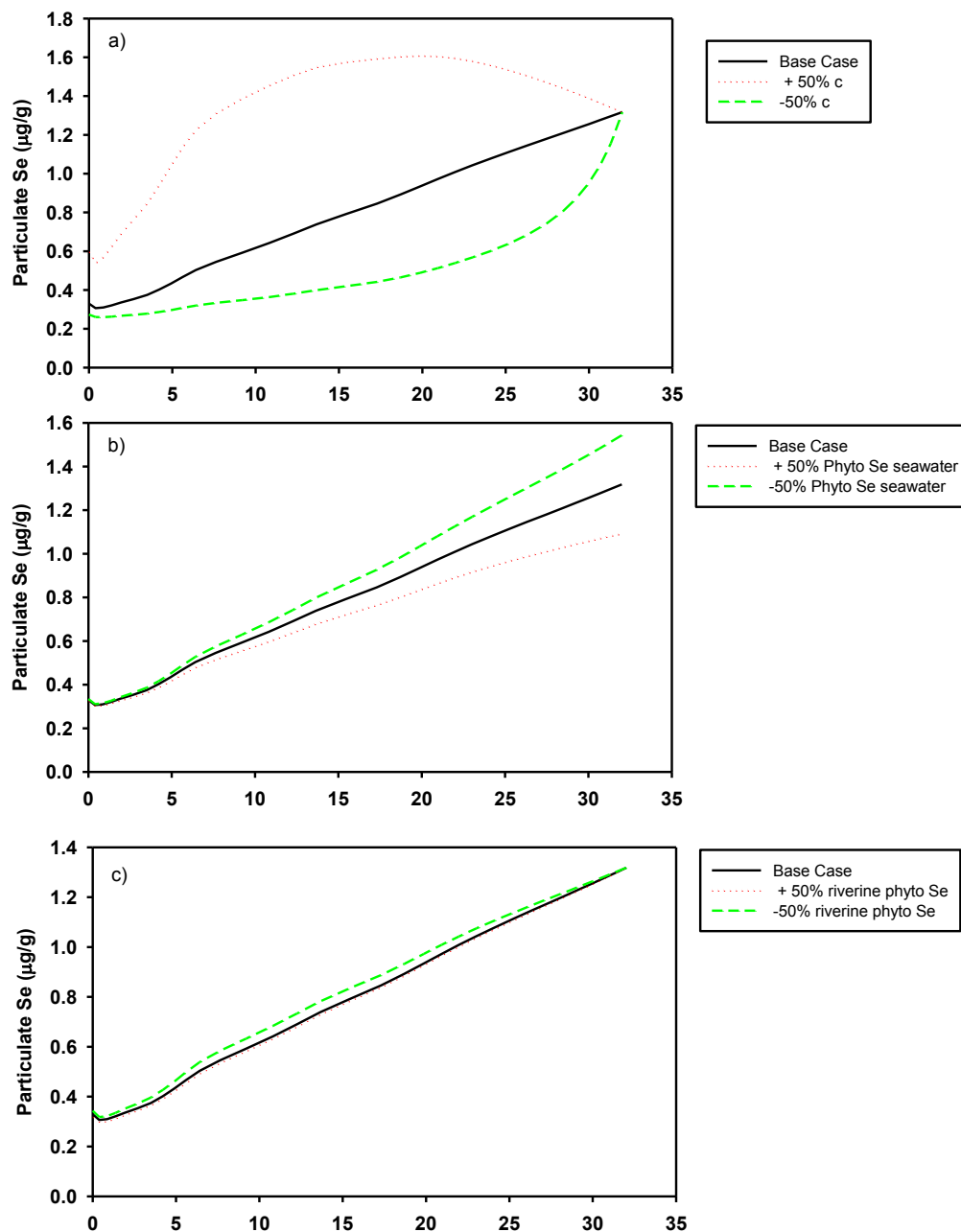


Figure 4-5 Modeled sensitivity of particulate selenium to changes in a) parameter *c* (factor that relate TSM concentration with flow), b) phytoplankton selenium in seawater and c) riverine phytoplankton selenium.

Of all the factors evaluated in this section, the sensitivity analysis highlights the need for detailed characterization of sources, including selenium speciation, to better capture conditions in the estuary. Although selenium speciation data have been reported for some time periods (Cutter and Cutter, 2004; Doblin et al., 2006), the vast majority of the data collection is in terms of total or dissolved selenium.

4.2. CHANGING CHLOROPHYLL A

The uptake of selenium by phytoplankton plays an important role in selenium transformation from the dissolved phase to the particulate phase. Some studies have shown possible increases in phytoplankton concentrations in the North San Francisco Bay in recent years (Cloern et al., 2007). A potential consequence of the increases in phytoplankton concentrations is an increase in particulate selenium concentrations (expressed in units of $\mu\text{g/g}$). The sensitivity of simulated particulate selenium concentrations (in $\mu\text{g/g}$) to increases in phytoplankton concentrations during low flow was tested through multiplying observed chlorophyll a concentrations in November 1999 (approximately $2 \mu\text{g/L}$) by a factor of 5, 10, and 15 (which result in average chlorophyll a concentrations approximating 10, 20 and $30 \mu\text{g/L}$). Model simulated selenium content on particulates can be as high as 1.2, 1.6 and $2.0 \mu\text{g/g}$ for chlorophyll a concentrations of 10, 20 and $30 \mu\text{g/L}$ (Figure 4-6). Mean selenium concentrations on particulates along the estuary was at 0.79, 0.94, 1.12, and $1.29 \mu\text{g/g}$ under chlorophyll a concentrations of 2, 10, 20, and $30 \mu\text{g/L}$, respectively. With the increase of chlorophyll a concentrations from $2 \mu\text{g/L}$ to 10, 20 and $30 \mu\text{g/L}$, estuarine mean selenium concentrations on particulates increased by 19.7%, 42.5% and 63.8%, respectively.

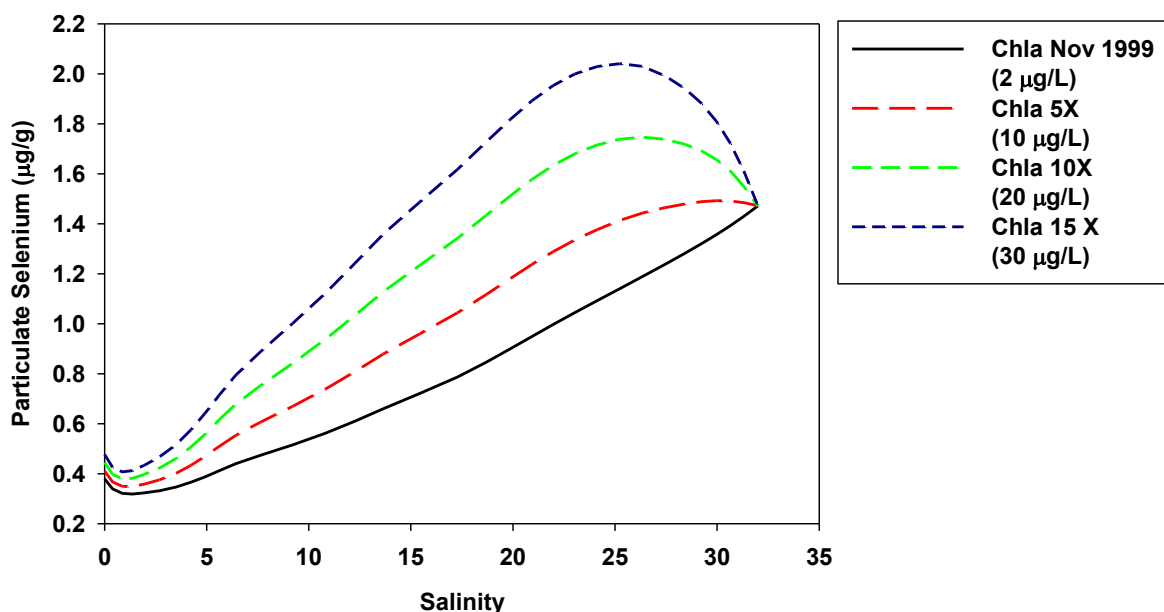


Figure 4-6 Simulated particulate selenium concentration (in $\mu\text{g/g}$) in response to different chlorophyll a concentration levels.

A test case using monthly estuary mean observed chlorophyll a concentrations in simulating phytoplankton uptake of selenium was run. The model was also run under the scenario of higher chlorophyll a concentration in seawater ($4 \mu\text{g/L}$). The results indicated differences in predicted particulate selenium concentrations, particularly under low flow, but generally showed good agreement among different chlorophyll a concentrations (Figure 4-7).

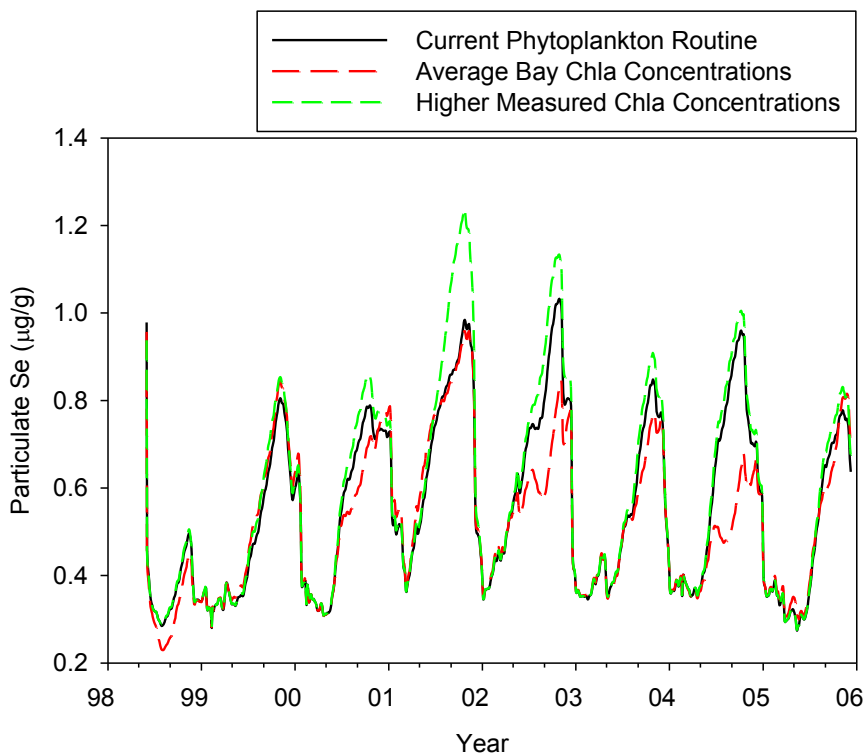


Figure 4-7 Simulated particulate selenium concentration (in $\mu\text{g/g}$) in response to different methods for simulating phytoplankton.

Overall, the tests varying chlorophyll a indicate the potential for significant impact to particulate concentrations. Indeed, highest chlorophyll a levels evaluated in Figure 4-6 have occurred in the Bay in the 1980s, and may do so again, depending on changing flows, temperature, and grazer abundance. However, in the range of concentrations now observed in the Bay and in the ocean, the differences due to chlorophyll a on particulate selenium are small, and the imperfections of the model calibration for chlorophyll a shown in Section 3 is unlikely to have had a major impact.

4.3. CALIBRATING UPTAKE AND MINERALIZATION BY PHYTOPLANKTON

The model parameterization presented in Section 3 used phytoplankton uptake and particulate organic selenide mineralization rate constants from the literature, following Meseck and Cutter (2006). These rate constants, were largely able to represent trends in dissolved and particulate selenium concentrations, as well as Se:C ratios in phytoplankton. The sensitivity of these rate constants was estimated by applying a $\pm 50\%$ change and discussed in Section 4.1. The model results for different selenium species were not found to be very sensitive over the range tested.

Given the importance of the uptake rates to the conversion of dissolved selenium to a form that can be readily assimilated by bivalves, and the paucity of literature values on uptake and mineralization rates of selenium, further exploration of these rate constants, going beyond the $\pm 50\%$ change, is helpful. If the model can be made to work with much higher uptake rates, it would imply a more rapid conversion of dissolved selenium to particulate selenium, and a more rapid response in particulate concentrations due to changing dissolved

concentrations. This is related to the ability to control bivalve uptake by controlling dissolved selenium concentrations in the bay.

The processes relating uptake of dissolved selenium species and the constituents constraining the calibration are shown in Figure 4-11. This is a subset of the all the selenium transformations considered in the model, and serves to explain the calibration of the uptake rate. In the testing that was performed, the uptake rate constants for selenite and dissolved organic selenide were raised by 10x and 100x their base calibration levels. In the base case calibration the selenate uptake rates were about 43% of the uptake rates for selenite. Selenate rates of uptake were not changed, because it is known that selenate uptake in a sulfate rich environment like NSFB is limited. As the model is currently set up, if the uptake rates are increased, there is an increase in the phytoplankton Se, and a decrease in the dissolved phase selenium concentrations. When the rate constants are increased by 10x and 100x, there is a depletion of the dissolved phase concentrations such that the observed data cannot be fit for Se(IV), Se(-II), and for the Se:C ratio in particulates. To fit the dissolved concentrations, and to prevent excessive buildup of Se in the phytoplankton compartment, the mineralization rate needs to be changed. The least squares best fits mineralization rates corresponding to the higher uptake rates are shown in Table 4-2. In effect, to fit the data, the mineralization rate needs to increase in the same proportion as the uptake rates; the 10x and 100x uptake rates correspond to similar increases in mineralization rate. A closer look at the dissolved phase data provides more insight into the processes. For the 10x case, the model fits for the dissolved phase are acceptable with a similar enhancement in mineralization rate. However, for the 100x case, even with the hundred-fold increase in mineralization rate, the fits for dissolved selenium are poor, and systematically different from the data. This exercise illustrates that the uptake rates are bounded to within a factor of 10 from the original calibration. Any increase in the uptake rates must be accompanied by an increase in the mineralization rate, such that the ratio of the uptake and mineralization is similar.

From the perspective of the TMDL, additional testing showed similar responses in bivalves to dissolved load changes for either the base case or the 10x uptake rate case, the latter associated with a 10x increase in mineralization rate. Thus, the base case uptake calibration is generally robust for application to the TMDL and for testing load changes in NSFB.

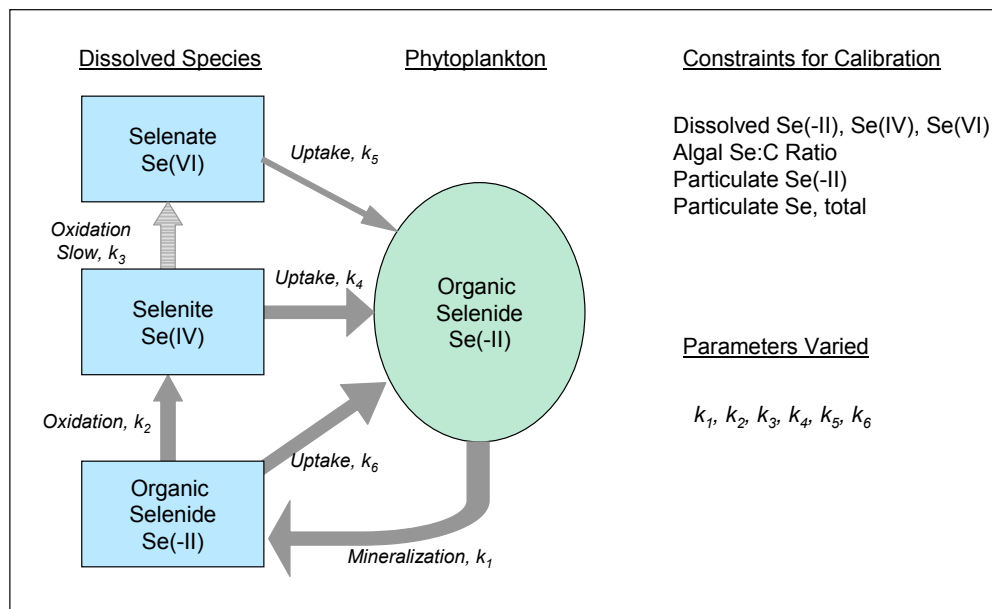


Figure 4-8 Processes related to phytoplankton uptake of various dissolved species, and mineralization to convert particulate organic selenide to dissolved organic selenide. Also shown are the different constituents that constrain calibration, and the parameters that may be varied to fit observed data.

Table 4-2
Changing Mineralization Rate as a Result of Changing Uptake Rates

	Uptake (l/ug Chla day)			Calibrated Mineralization Rate (1/day) k1 (POrgSe)
	k4 (SeIV)	k5 (SeVI)	k6 (Se-II)	
Base Case	0.000379	0.000081	0.000189	0.00657
10x	0.003787	0.000081	0.001894	0.0592
100x	0.037872	0.000081	0.018936	0.666

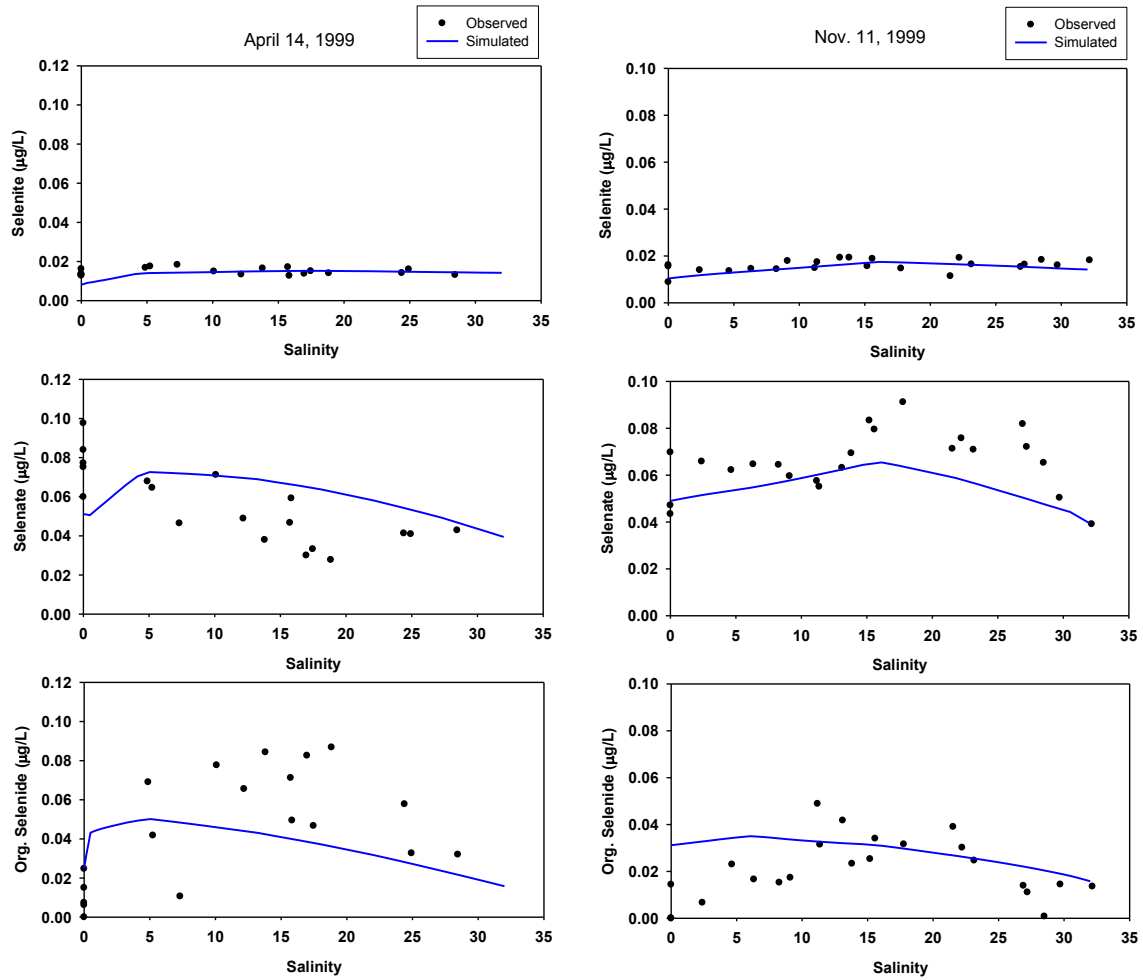


Figure 4-9 Dissolved phase selenium concentrations when uptake rates for selenite (Se(IV)) and selenide (Se(-II)) are raised by a factor of 10 from their base case values. The best fit to data was by least squares minimization, and resulted in mineralization rates that were higher than base case rates by a factor of 10 as well.

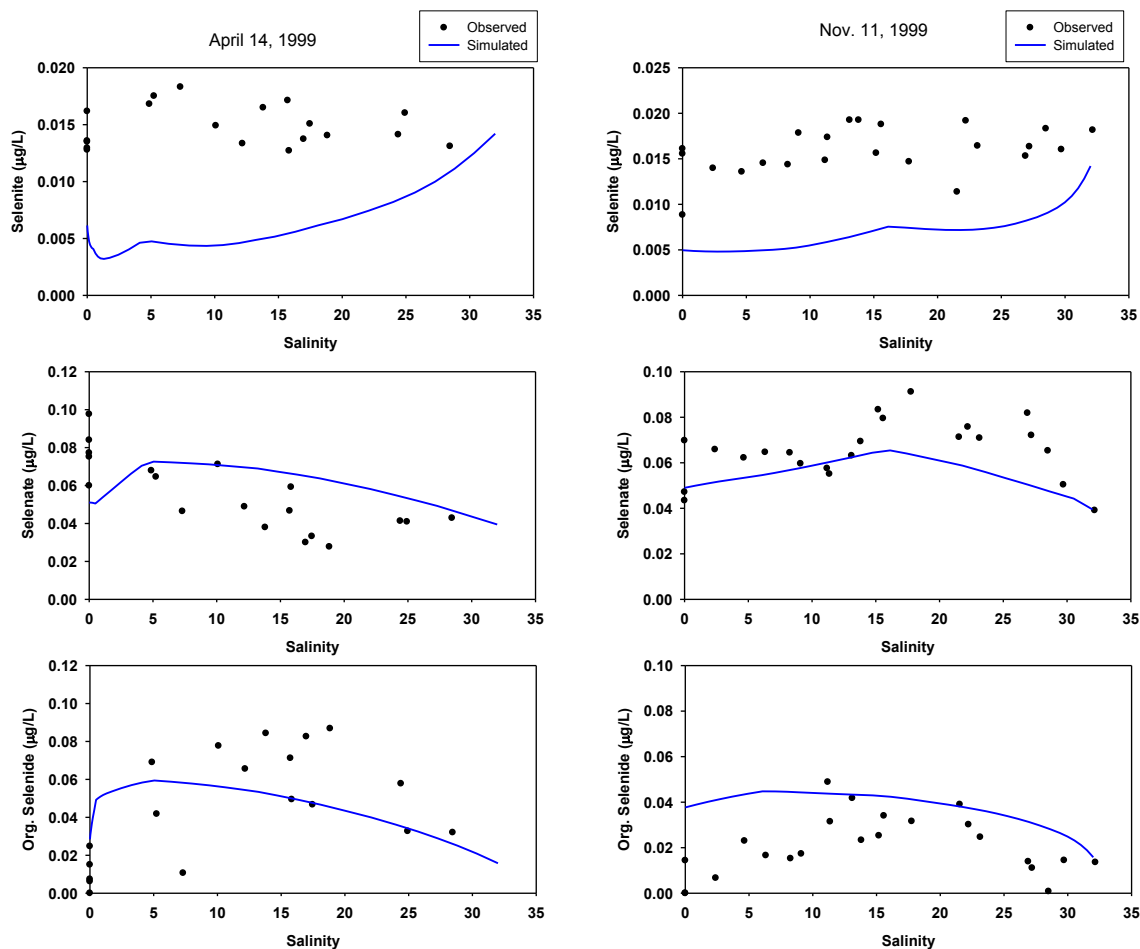


Figure 4-10 Dissolved phase selenium concentrations when uptake rates for selenite (Se(IV)) and selenide (Se(-II)) are raised by a factor of 100 from their base case values. The best fit to data was by least squares minimization, and resulted in mineralization rates that were higher than base case rates by a factor of 100 as well. However, even with this change, the selenite was significantly depleted compared to the data, suggesting that this uptake rate is too high.

4.4. VARYING SEAWATER AND RIVERINE BOUNDARY PARTICULATE SELENIUM CONCENTRATIONS

4.4.1 Lowering Seawater Endmember

Particulate selenium concentrations in the seawater endmember are not well defined. The approach used in Section 3 is to calibrate using field data. This resulted in a seawater boundary value of $1.22 \mu\text{g/g}$, which may be compared with a reported value by Cutter and Bruland (1984) of $1.69 \mu\text{g/g}$ at a depth of 50m in the Pacific Ocean. An alternative is to use particulate selenium concentrations measured at Golden Gate by Doblin et al. (2006) as the seawater endmember concentrations for particulate selenium, ($\sim 0.9 \mu\text{g/g}$). This boundary values results in simulated particulate selenium concentrations are lower, particularly near the mouth of the estuary (Figure 4-11).

Simulated selenium concentrations in bivalves over long-term periods show some difference from the original simulation. Simulated selenium concentrations in bivalves at Carquinez Strait are slightly lower than in the original simulation. The difference is more evident

during low flow, with the largest difference up to 1 $\mu\text{g/g}$ (Figure 4-12). With the lower seawater end member concentration, simulated particulate selenium concentrations in $\mu\text{g/L}$ still compared reasonably well to the observed data (Figure 4-13 and Figure 4-14).

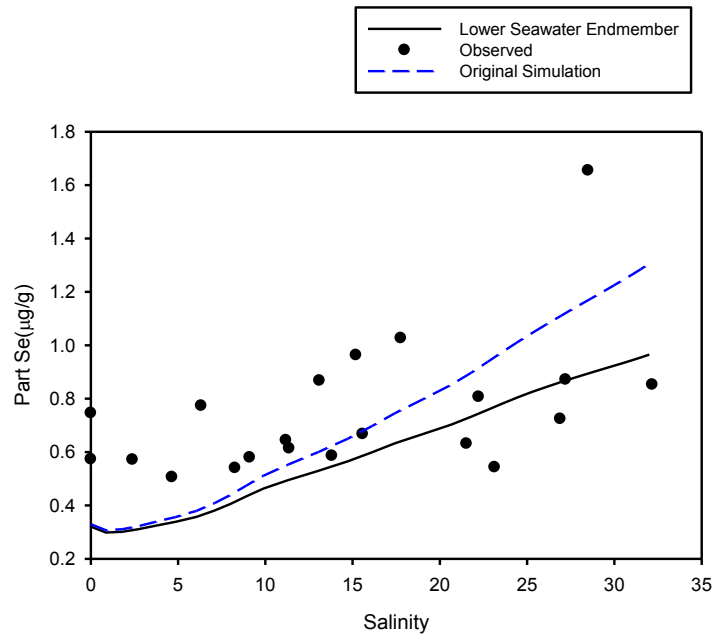


Figure 4-11 Model simulated particulate selenium using lower seawater endmember for a low flow period (November 1999), compared to original simulation.

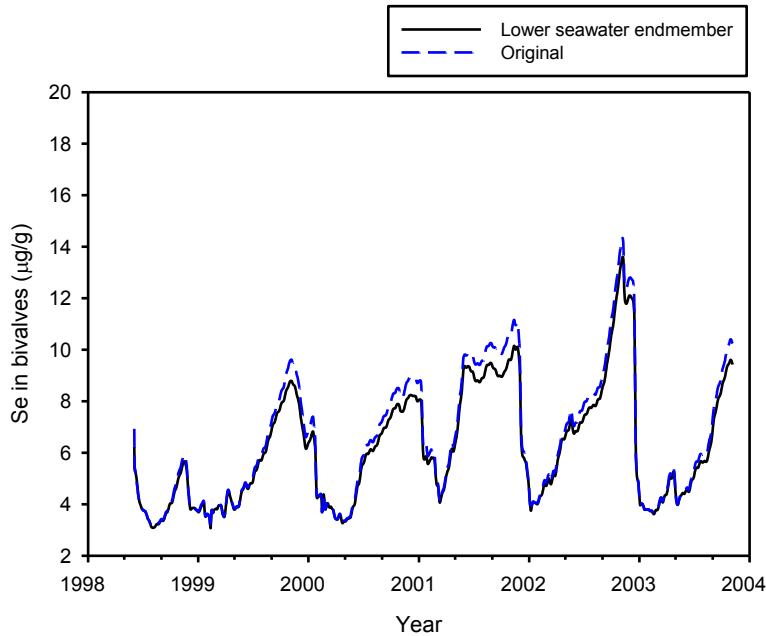


Figure 4-12 Model simulated selenium concentrations in bivalves using lower seawater end member, compared to the original simulation.

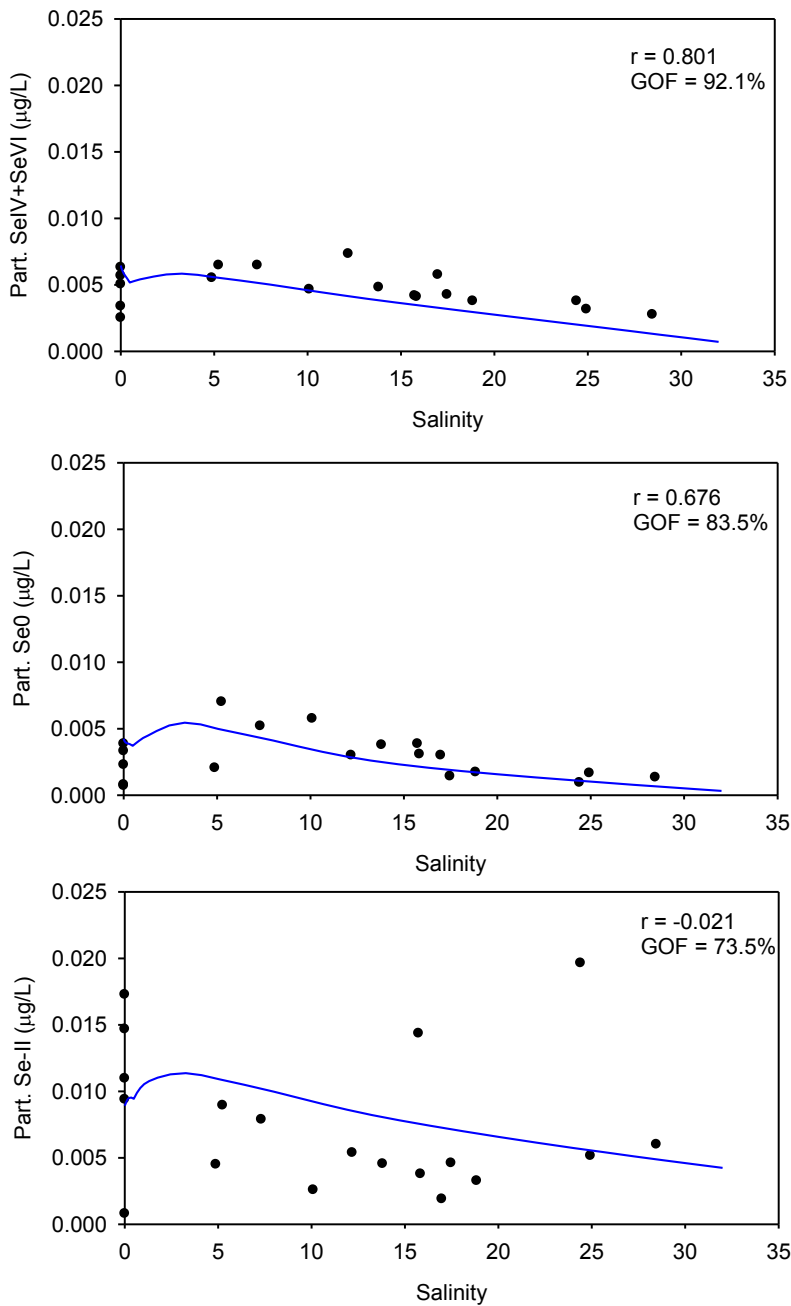


Figure 4-13 Model simulated particulate selenium concentrations (in µg/L) using lower seawater endmember particulate selenium concentration for high flow period (April, 1999).

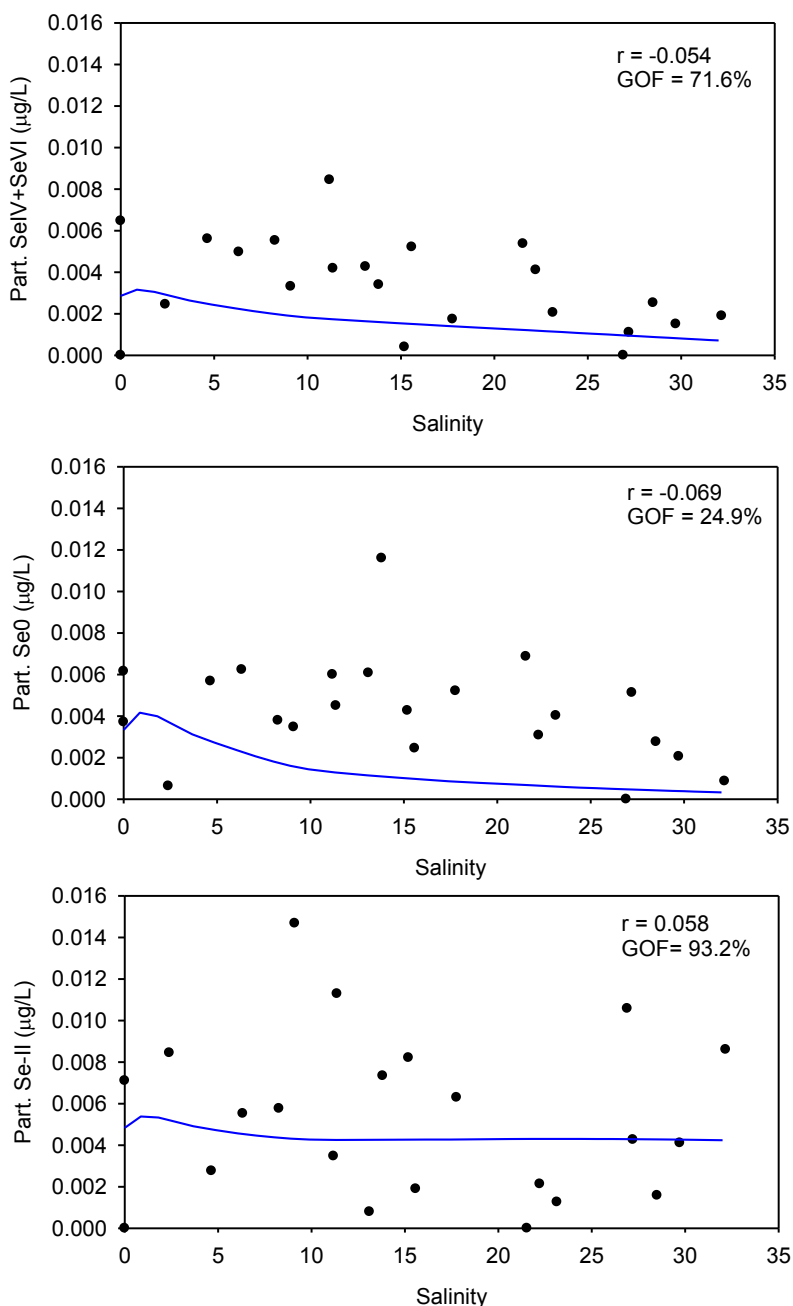


Figure 4-14 Model simulated particulate selenium concentrations (in µg/L) using lower seawater endmember particulate selenium concentration for a low flow period (November, 1999).

4.4.2 Impacts of Varying Riverine Endmember Concentrations

Particulate selenium concentrations at the riverine endmember measured by Doblin et al. (2006) ranged from 0.08-0.40 µg/g for particulate elemental selenium, 0.25 µg/g for particulate selenite and selenate and 0.015-0.74 µg/g for particulate organic selenide. Total particulate selenium concentrations also show some variation ranging from 0.357 to 0.747 µg/g at Rio Vista (n = 4; Doblin et al. 2006). For the calibration period of 1999, riverine

particulate selenium concentrations for different species were determined through calibration. The calibration objective was to derive the riverine particulate selenium concentrations that result in best fit of particulate selenium species (in $\mu\text{g/L}$) with the observed data. To evaluate the effects of varying riverine particulate selenium concentrations in model predictions, high and low riverine endmember selenium concentration scenarios were formulated. The high and low riverine particulate selenium scenarios were formed through specifying upper bound and lower bound of particulate selenium concentrations associated with PSP, BEPS and phytoplankton, respectively.

To test the impact of varying riverine particulate selenium concentrations associated with PSP, BEPS and phytoplankton, the higher and lower bounds of particulate selenium concentrations associated with PSP (mean \pm standard deviation) based on observed data in Sacramento River at Rio Vista were used (for PSe0 and PSeivvi). For particulate organic selenide, the minimum and maximum particulate organic selenide concentrations were used.

For Se:C uptake ratios measured in the Delta, Se:C uptake ratio for bacteria is higher at about 32 $\mu\text{g/g}$, and Se:C uptake ratios by phytoplankton are about 11 $\mu\text{g/g}$. These values were used in specifying higher and lower end of particulate selenium associated with phytoplankton. Selenium concentrations on particulates used in testing the effects of riverine boundary conditions are listed in Table 4-3.

Table 4-3
Upper and Low Bound of Particulate Selenium Concentrations Used in Riverine Endmembers

	PSP (PSeivvi)	PSP (PSe0)	PSP (POrgSe)	PSP (total Part. Se)	BEPS (total Part. Se)	Se:C ratio in riverine phytoplankton
Upper bound ($\mu\text{g/g}$)	0.257	0.407	0.740	1.404	0.269	31.80
Lower bound ($\mu\text{g/g}$)	0.041	0.132	0.015	0.188	0.054	11.13

The use of higher and lower bounds of riverine endmember particulate selenium concentrations result in simulated particulate selenium concentrations in the estuary (in $\mu\text{g/g}$) to be significantly different from the base case (Figure 4-15). Simulated selenium concentrations in bivalves over the long-term are also significantly different from the base case (Figure 4-16).

The changes in riverine end member concentrations of particulate selenium have some impacts on simulations of particulate selenium concentrations (in $\mu\text{g/L}$) during high flow, with predicted particulate selenium greater than observed using the higher boundary condition. Simulated particulate selenium concentrations (in $\mu\text{g/L}$) during low flow compared reasonably to both low and high riverine boundary conditions (Figure 4-17), a reflection of the substantial variability in the particulate selenium data in the bay. The model predictions of particulate selenium ($\mu\text{g/l}$) for high flow conditions, do not compare well to the data for the higher riverine boundary condition.

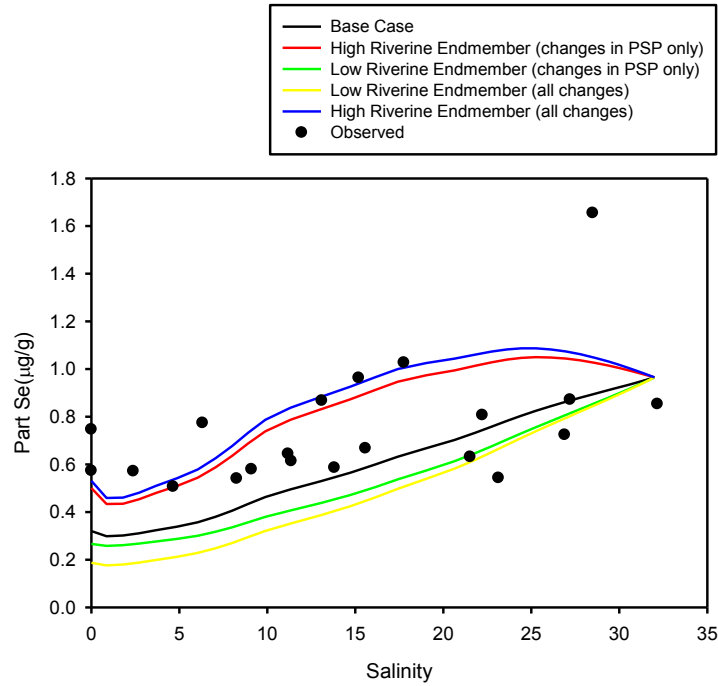


Figure 4-15 Simulated particulate selenium concentrations (in µg/g) using higher and lower particulate selenium concentrations in the riverine end member.

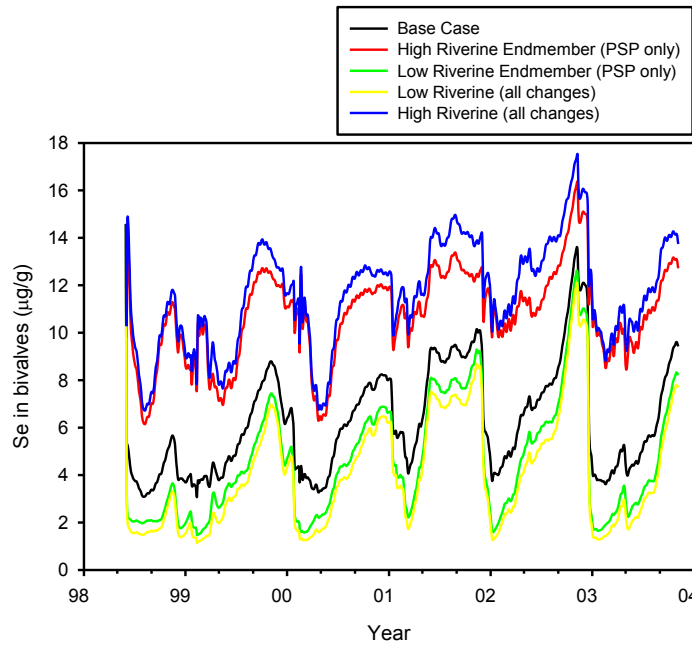


Figure 4-16 Simulated selenium concentrations in bivalves using higher and lower riverine end member concentrations of particulate selenium.

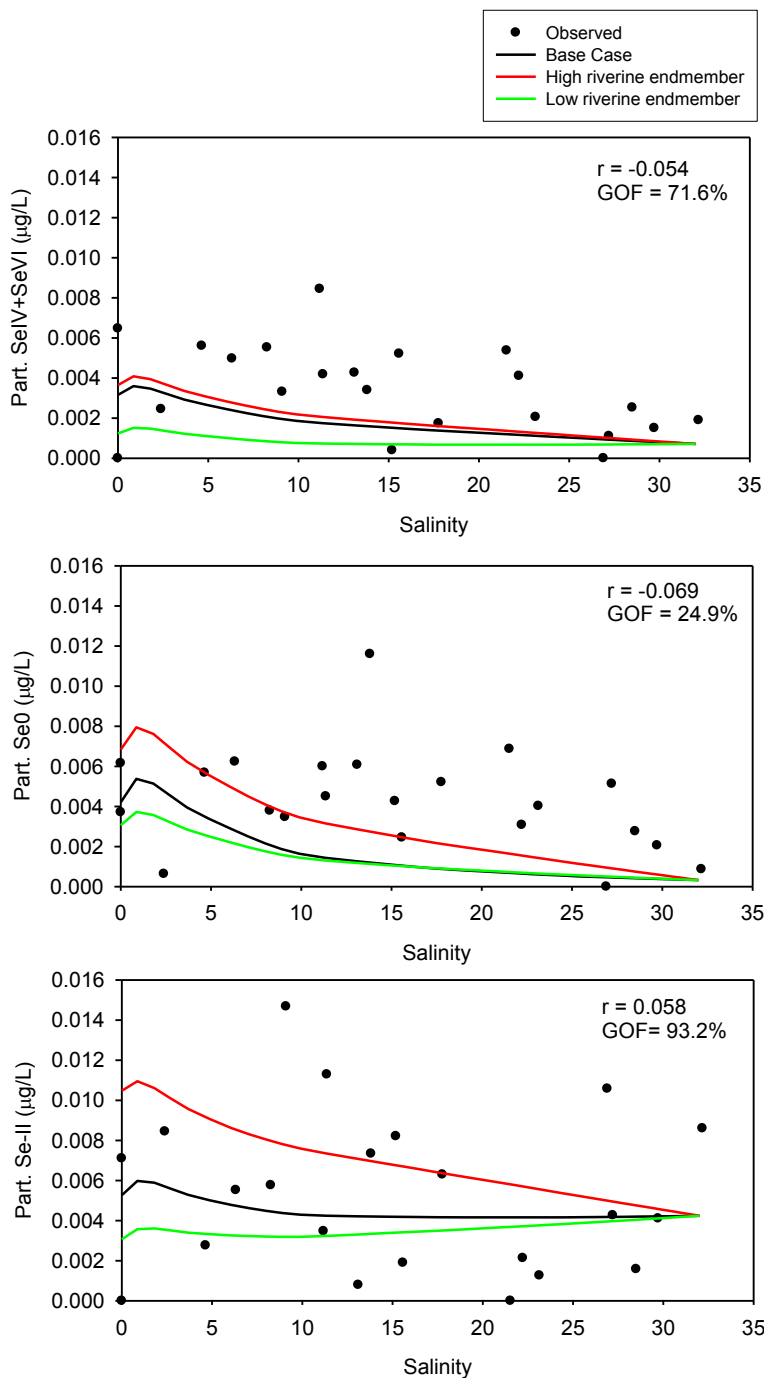


Figure 4-17 Model simulated particulate selenium concentrations (in $\mu\text{g/L}$) under a low flow period (November, 1999) using higher and lower riverine end member concentration of particulate selenium.

4.4.3 Higher and Lower Bounds of Riverine and Seawater Endmember Concentrations

Based on the preceding presentation of varying seawater and riverine boundary values, and the limited data available to define each boundary, a lower and higher boundary of riverine particulate selenium concentrations can be used to add more robustness to the model predictions (Table 4-4). The use of a higher riverine boundary condition resulted in

significant over-predictions in particulate selenium ($\mu\text{g/l}$) during high flow, the higher boundary condition was only applied for the lower flow conditions (defined as $\text{NDOI} < 1.5 \times 10^{10}$ l/d). Two different particulate selenium concentrations in the seawater endmember could also be used. The resulting estuarine particulate selenium during a low flow period (November 11, 1999) using the lower and higher boundary riverine and seawater endmember concentrations are able to better capture the range in the observed data (Figure 4-18).

The model predicted selenium concentrations in bivalves using the lower and higher riverine and seawater boundary conditions are shown in Figure 4-19. The range of boundary conditions will be used when the model is run in a predictive mode

Table 4-4
Lower and Higher Boundary of Riverine and Seawater Endmember Concentrations

	Riverine Boundary			Seawater Boundary	
	PSP PSe ($\mu\text{g/g}$)	BEPS PSe ($\mu\text{g/g}$)	Se:C in phytoplankton ($\mu\text{g/g}$)	PSP PSe ($\mu\text{g/g}$)	Se:C in phytoplankton ($\mu\text{g/g}$)
Lower Boundary	0.46	0.25	15.9	0.96	21.0
Higher Boundary (Applied when $\text{NDOI} < 1.5 \times 10^{10}$ l/d)	0.75	0.50	15.9	1.22	21.0

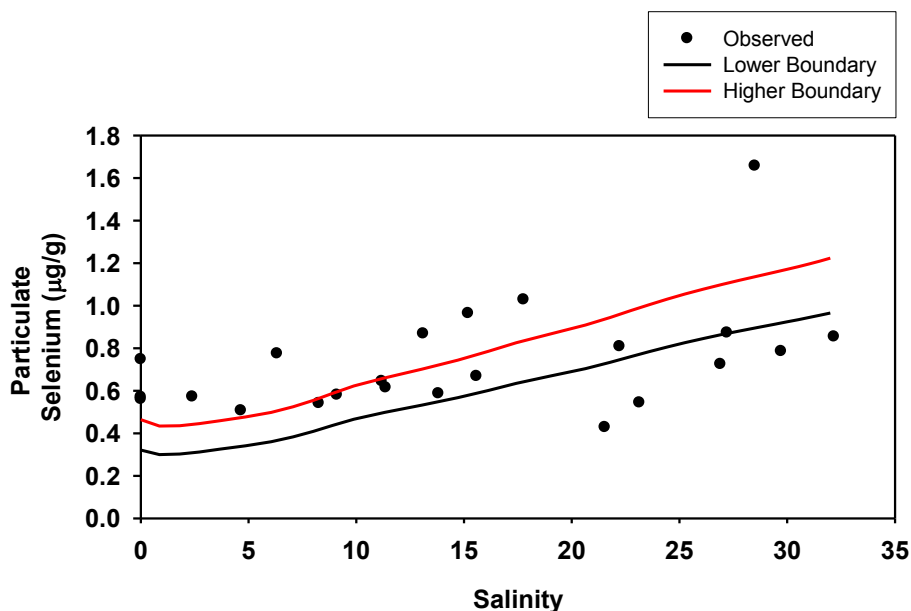


Figure 4-18 Model simulated particulate selenium concentrations under upper and lower bounds of riverine and seawater endmember concentrations.

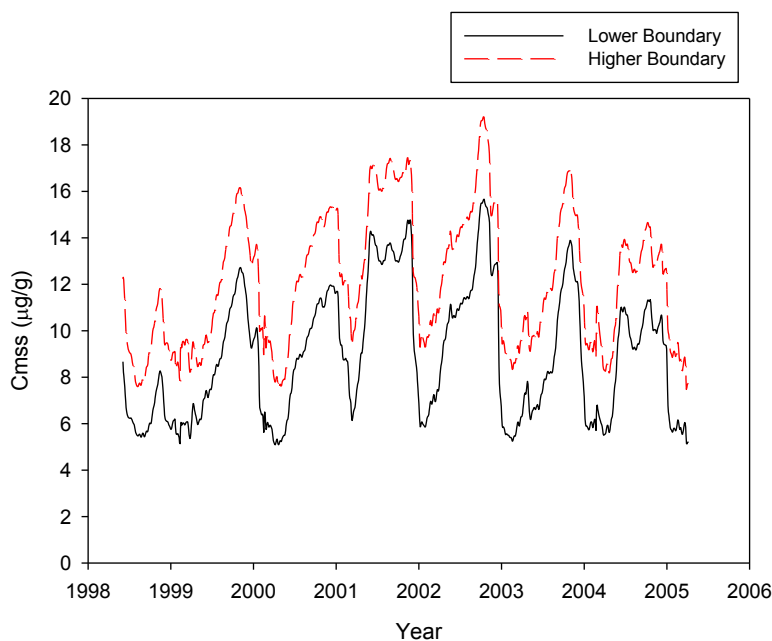


Figure 4-19 Model simulated particulate selenium concentrations under upper and lower bounds of riverine and seawater endmember concentrations.

4.5. RELATIVE CONTRIBUTION OF DIFFERENT SOURCES OF PARTICULATE SELENIUM

Particulate selenium is the primary uptake route of selenium by the bivalves. Different species of particulate selenium have different assimilation efficiencies. Particulate selenium can originate from the bed sediment (BEPS), the riverine input (PSP) and *in situ* transformation (phytoplankton uptake) and species composition may be different for these sources. A better understanding of the contribution of particulate selenium from these sources can help determine the effectiveness of management actions to be taken (whether emphasis can be placed on riverine particulate selenium or selenium from bed sediments or reducing phytoplankton uptake by reduced dissolved selenium input).

Particulate selenium concentrations here are expressed both in $\mu\text{g/L}$ and $\mu\text{g/g}$. For a low flow period, over the estuary, model simulated permanently suspended particulate (PSP) associated selenium comprises the largest portion of particulate selenium (Figure 4-20). Phytoplankton associated selenium is approximately half of the PSP associated selenium. Particulate selenium contribution from BEPS decreases from the head of the estuary, a pattern similar to TSM. For a specific location (Carquinez Strait), simulated time series of particulate selenium concentrations again indicated PSP selenium accounts for the largest portion of particulate selenium (Figure 4-21). All sources of particulate selenium appear to increase during high flow. During low flow, simulated phytoplankton associated selenium could be more significant than BEPS associated selenium. Overall, the composition of simulated estuary mean particulate selenium for November 11, 1999 is nearly 50% of permanent suspended particulates (PSP), with phytoplankton associated particulate selenium and particulate selenium associated with bed exchange materials accounting for 25% each (Figure 4-22).

In terms of loading, riverine inputs (TSM), are the largest source of particulate selenium loads to the estuary, followed by phytoplankton uptake (Figure 4-23). Due to the relatively balanced sediment erosion and deposition, net particulate selenium loadings from the estuary are small.

A few cases were run to test the effects of each individual source of particulate selenium on predicted particulate selenium (in $\mu\text{g/g}$). These are a case with removal of all riverine inputs of particulate selenium, a case assuming no selenium uptake by phytoplankton and no riverine phytoplankton input, and a case with no sediment-water exchange. The results are shown in Figure 4-24 and Figure 4-25. For a low flow period (November 11, 1999), removing bed exchange processes results in a small change in predicted particulate selenium. Assuming no phytoplankton uptake of selenium results in a decrease in particulate selenium along the estuary, due to mineralization of particulate organic selenium to dissolved organic selenide and dilution (or mixing) by seawater. Assuming no riverine inputs of particulate selenium, particulate selenium concentration at low to mid-salinities is about one-third of the original concentrations, although the differences become smaller with proximity to the seawater boundary.

Predicted particulate selenium concentrations (Figure 4-24 and Figure 4-26) indicated that net bed exchange contributes a small portion of the particulate selenium along the estuary. Uptake by phytoplankton accounts for a larger portion of the particulate selenium. Phytoplankton uptake plays an important role in maintaining high particulate selenium concentrations in the San Pablo Bay and Central Bay. Particulate selenium inputs from the rivers contribute to the largest portion of the particulate selenium. Riverine inputs of the particulate selenium are mostly comprised of more bio-available particulate organic selenide and particulate selenite + selenate. Phytoplankton uptake results in particulate organic selenide that is readily assimilated by clams. As for the TMDL, reductions in riverine inputs of particulate selenium or phytoplankton-associated selenium are likely to have a greater effect in achieving lower selenium concentrations in bivalves.

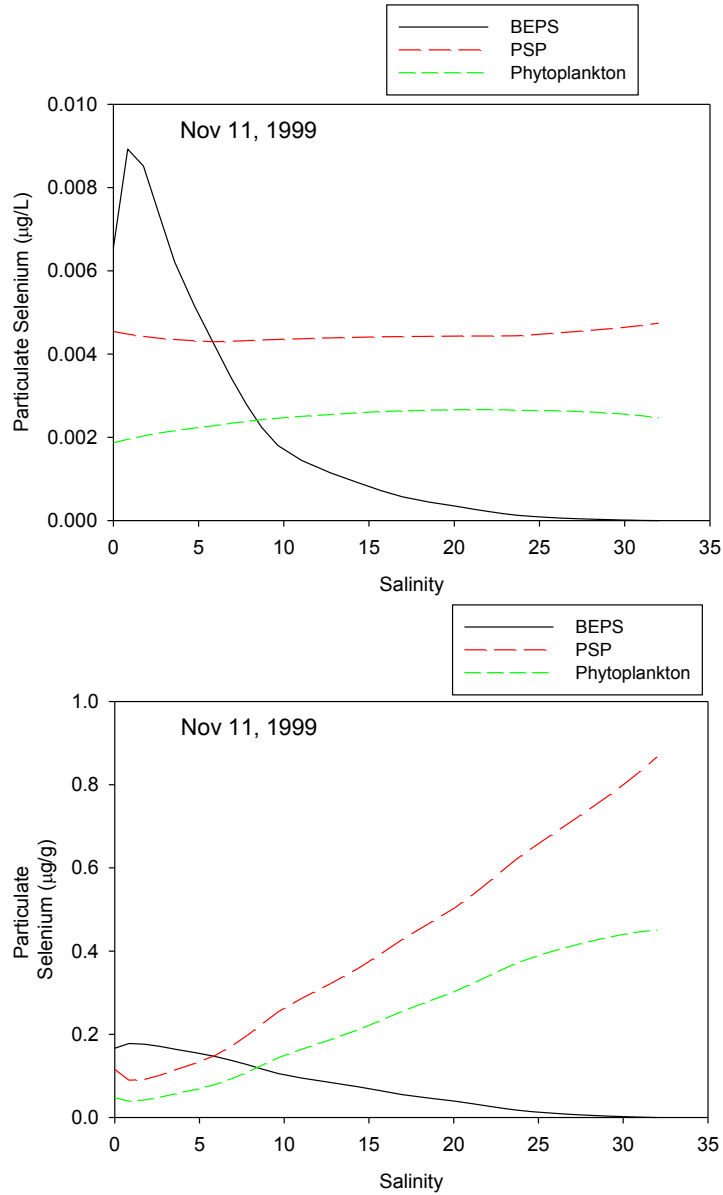


Figure 4-20 Particulate selenium along the salinity gradient as contributions from permanently suspended particulates (PSP), bed exchange particulates (BEPS) and phytoplankton for a low flow period (November 11, 1999). Riverine particulate selenium: 0.467 µg/g, Seawater particulate selenium: 1.22 µg/g.

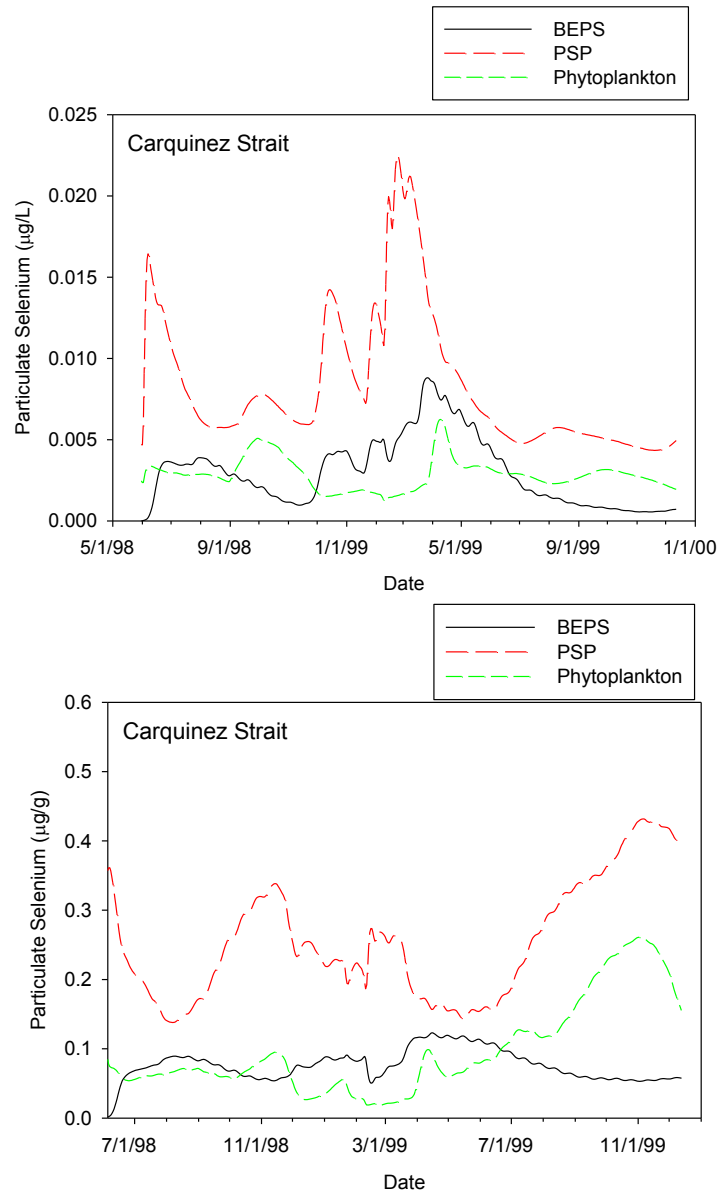


Figure 4-21 Particulate selenium at Carquinez Strait (X = 47,439 m from Rio Vista) over time as contributions from permanently suspended particulates (PSP), bed exchange particulates (BEPS) and phytoplankton⁴.

⁴ Particulate Se in phytoplankton is dominated by organic Se. Se in PSP and BEPS can be comprised of adsorbed selenite and selenate, elemental selenium and organic Se.

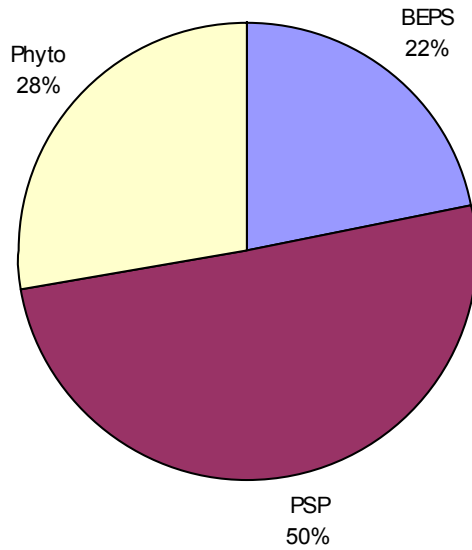


Figure 4-22 Contribution of different sources to the mean particulate selenium concentrations in NSFB for November 11, 1999.

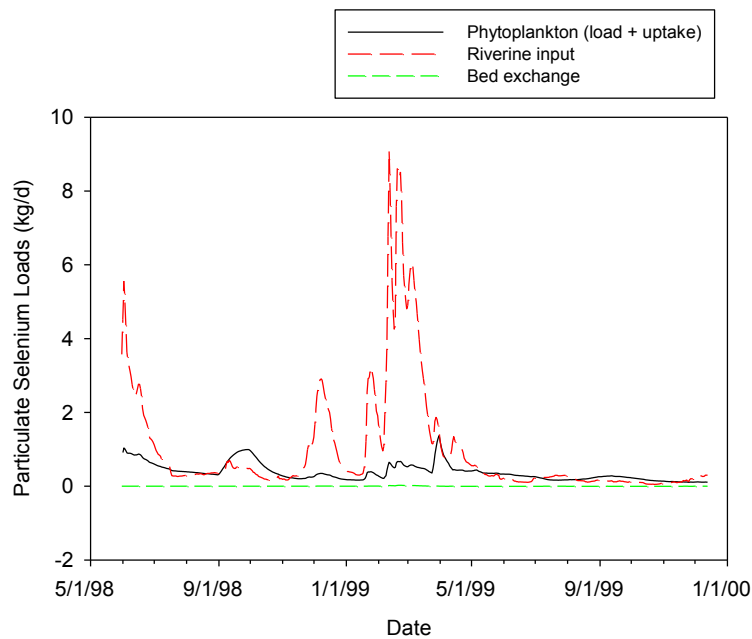


Figure 4-23 Model predicted particulate selenium load inputs from riverine input, phytoplankton uptake and bed exchange.

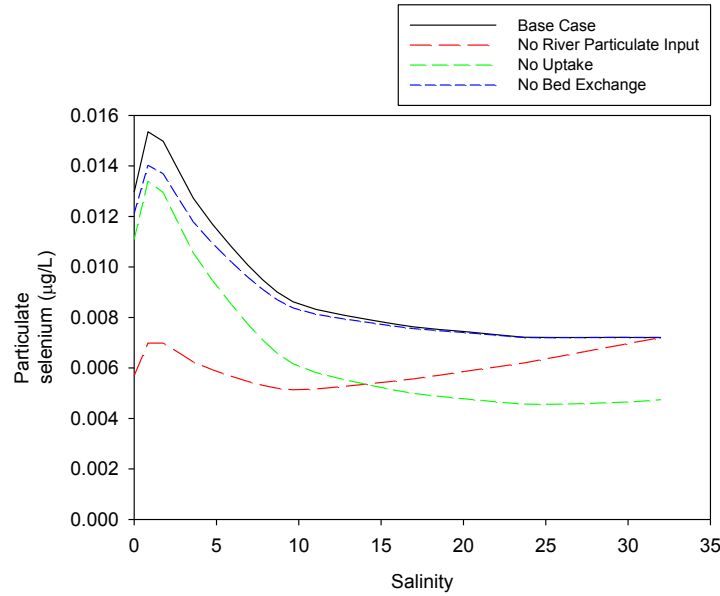


Figure 4-24 Model predicted particulate selenium concentrations (in µg/L) under scenarios of no riverine particulate selenium input, no phytoplankton uptake, and no bed exchange.

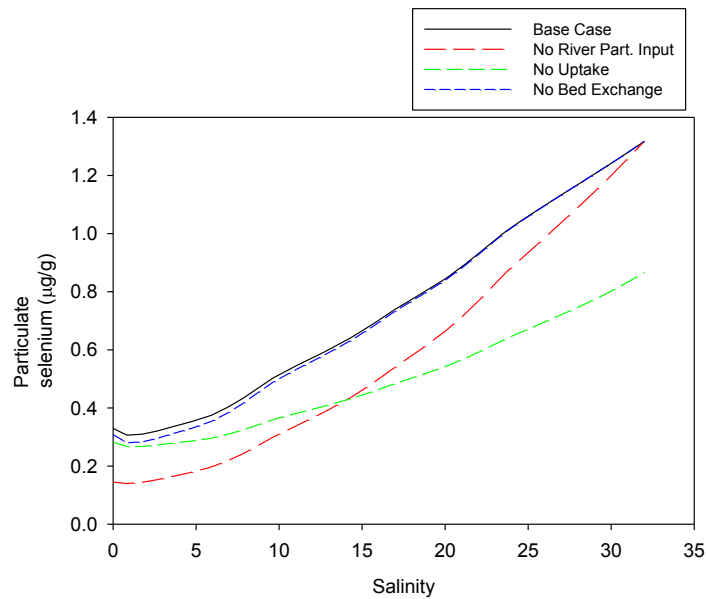


Figure 4-25 Model predicted particulate selenium concentration (in µg/g) under scenarios of no riverine particulate selenium input, no phytoplankton uptake and no bed exchange.

4.6. MASS BALANCE OF SELENIUM

Annual budgets of dissolved and particulate selenium suggested that outflow from the Bay is the largest loss mechanism (Figure 4-26 and Figure 4-27). For the water years simulated, outflow of dissolved and particulate selenium balances selenium input from all sources including riverine input and local point sources. For some years selenium was gained in storage in the water column, but was lost in the next year.

Bacteria, algae and plants can form dimethylselenide and dimethyldiselenide that can be volatilized to the atmosphere (Ansele and Yoch, 1997). Dimethylselenide loss to the atmosphere can be up to 30% in the wetland/marsh systems (Zhang and Moore, 1997; Hansen et al., 1998). Volatilization of selenium in open water ecosystems (e.g., in bays) is less well known. For the purpose of this analysis, volatilization was not considered to be a significant loss mechanism.

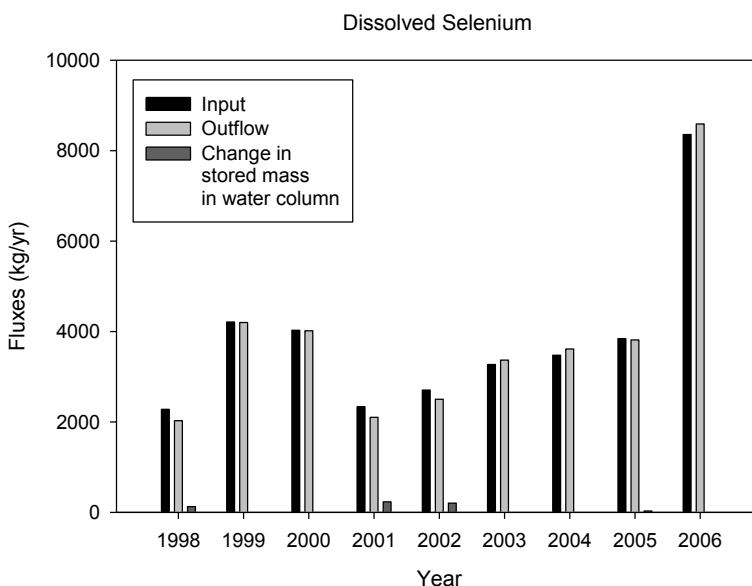


Figure 4-26 Model simulated mass balance of dissolved selenium for the period of 1998-2006

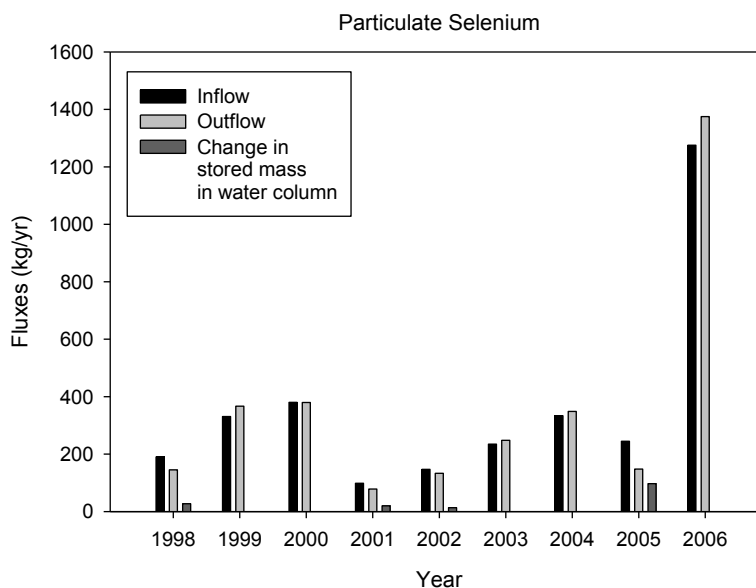


Figure 4-27 Model simulated mass balance of particulate selenium for the period of 1998-2006

A more detailed conceptual diagram of sources and sinks of dissolved and particulate selenium are shown for water years 1999, 2005, and 2006 for the NSFB (Figure 4-28 to Figure 4-33). Dissolved selenium loads from the San Joaquin River are approximately equal

to the Sacramento River input. Local tributaries represent the second largest inputs of dissolved selenium following the riverine inputs, followed by refinery loads and POTWs. Tributary and refinery loads show some variation among the years. The South Bay represents a larger input of dissolved selenium than POTWs. The overall load inputs of dissolved selenium are approximately equal to outflow to ocean water.

For particulate selenium, riverine inputs from Sacramento River at Rio Vista vary by a factor of 1.5 depending on the riverine boundary condition used. Overall particulate selenium inputs from the Sacramento River at Rio Vista were much higher than inputs from the San Joaquin River at the confluence (by a factor of approximately 7). Outflow of particulate selenium to the ocean was approximately equal to loads of particulate selenium. In current version of the model, particulate selenium loads from the refineries and the tributaries were assumed to be zero. The model predicted net outflow of particulate selenium from bed sediment (loss of particulate selenium associated with BEPS) ranged from 17.7 kg/yr in 2005 to 115.2 kg/yr in 2006, and were lower than the previous estimate of loss of 285 kg/yr due to net sediment erosion in TM2. This is likely due to the fact that the model is currently under-predicting the active bed sediment mass.

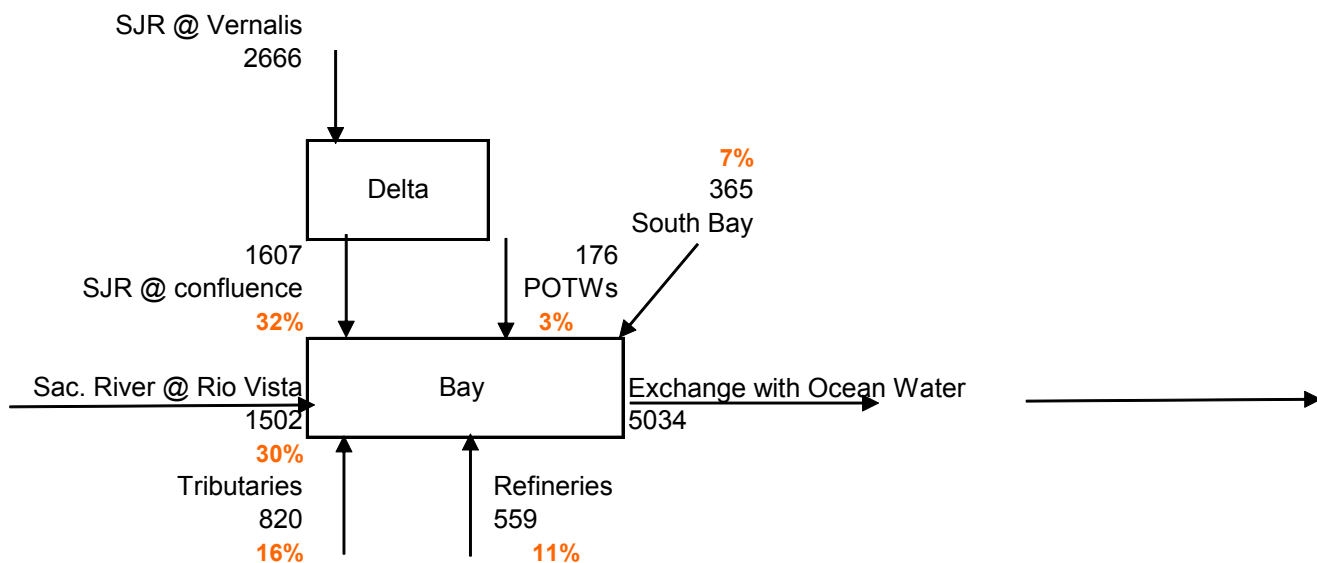


Figure 4-28 Sources and sinks of dissolved selenium in the NSFB for water year 1999 (kg/yr). Percentages of each source contributing to total load are also shown.

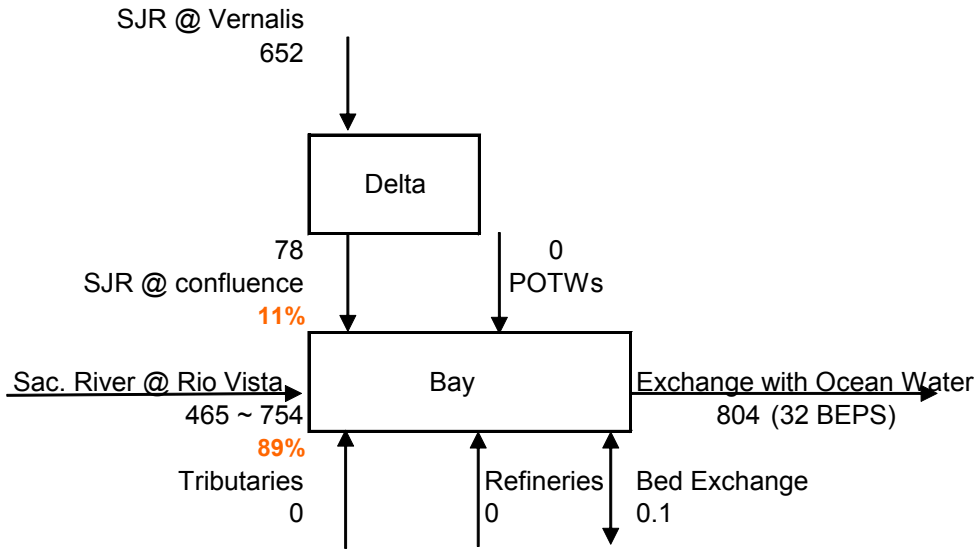


Figure 4-29 Sources and sinks of particulate selenium in the NSFB for water year 1999 (kg/yr). Loads are also shown as a percentage of combined Sacramento and San Joaquin River load.

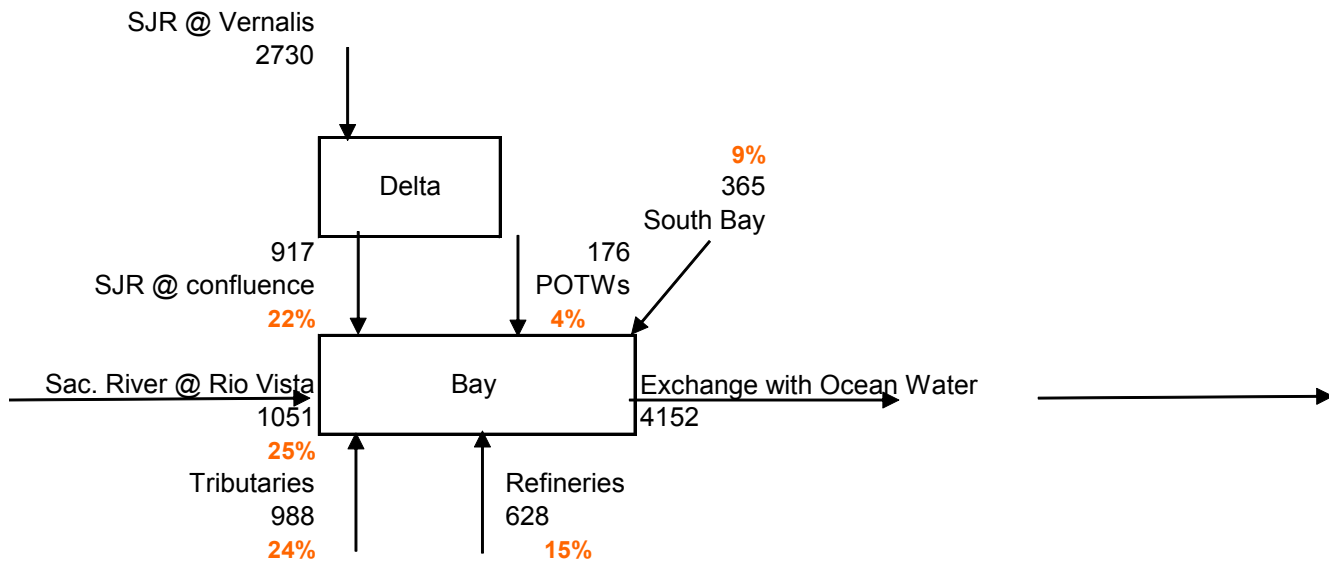


Figure 4-30 Sources and sinks of dissolved selenium in the NSFB for water year 2005 (kg/yr). Percentages of each source contributing to total load are also shown.

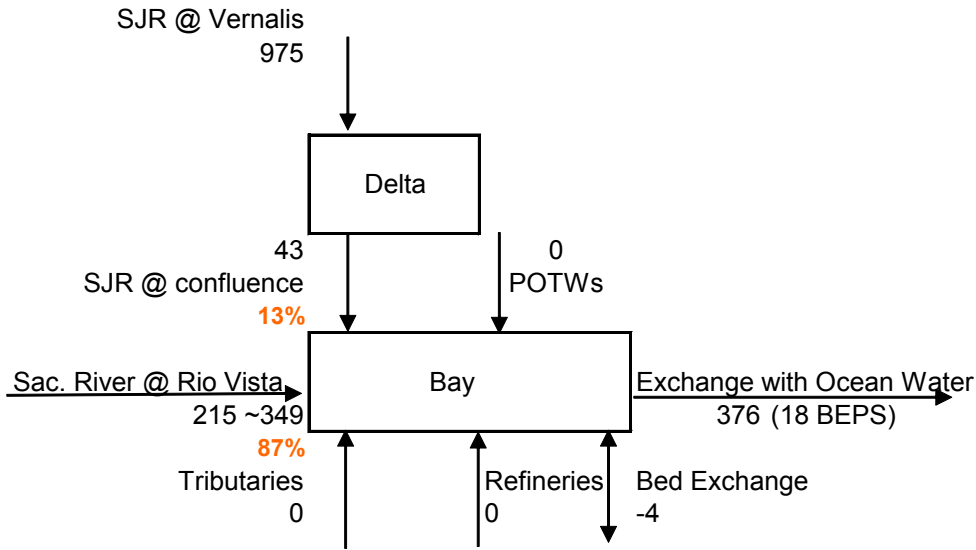


Figure 4-31 Sources and sinks of particulate selenium in the NSFB for water year 2005 (kg/yr). Loads are also shown as a percentage of combined Sacramento and San Joaquin River load.

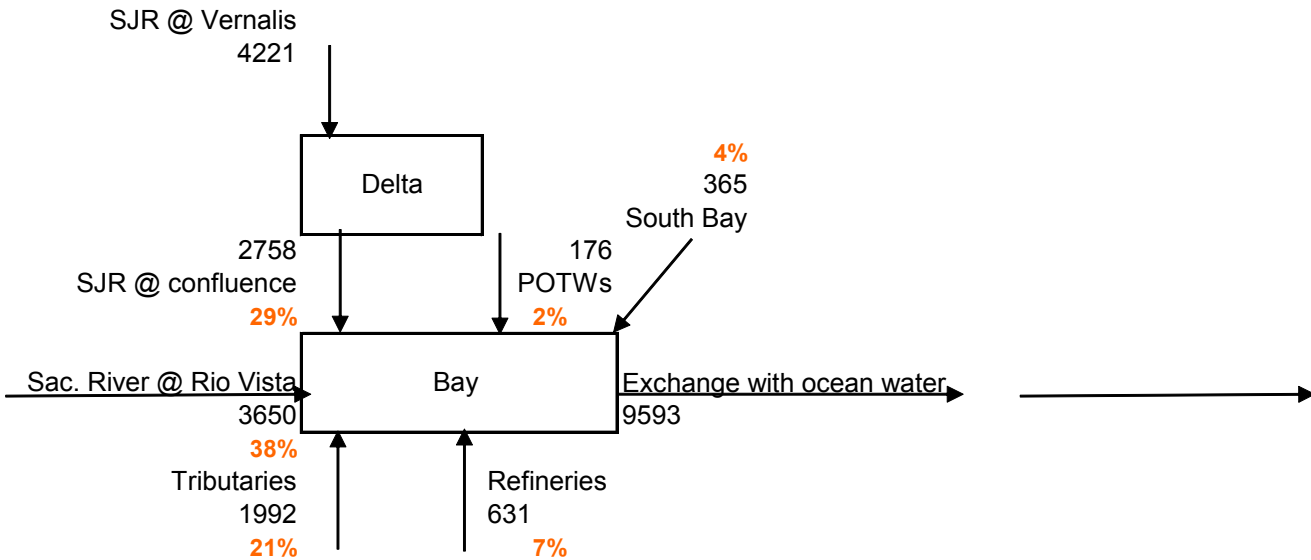


Figure 4-32 Sources and sinks of dissolved selenium in the NSFB for water year 2006 (kg/yr). Percentages of each source contributing to total load are also shown.

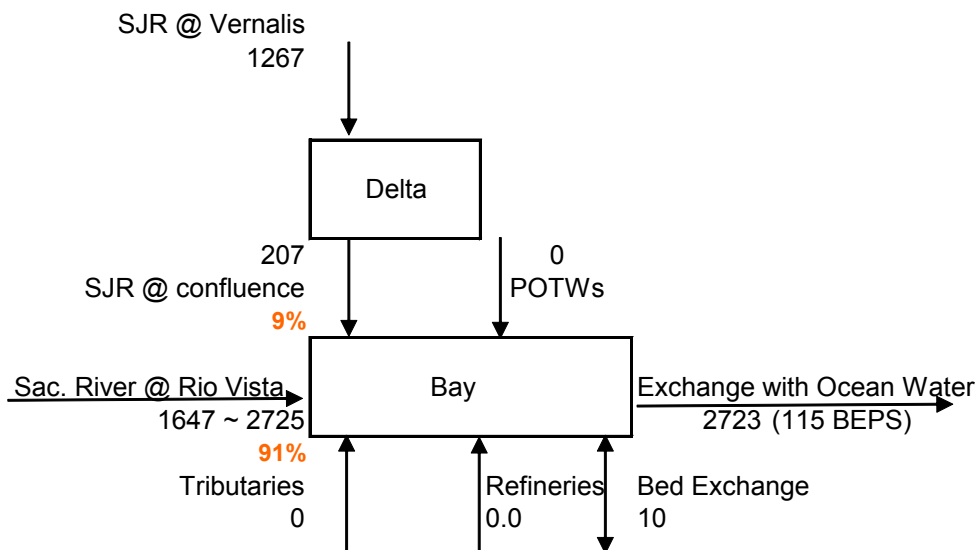


Figure 4-33 Sources and sinks of particulate selenium in the NSFB for water year 2006 (kg/yr). Loads are also shown as a percentage of combined Sacramento and San Joaquin River load.

Standing stocks of different species of selenium in the Bay are relatively constant on an annual basis but show seasonal variability due to variation in riverine and tributary input (Figure 4-34 and Figure 4-35). Dissolved selenium standing stock is comprised mostly of selenate, followed by organic selenide and selenite. Particulate organic selenide contributes to the largest percentage of the standing stock in particulate selenium, followed by particulate selenite and selenate, and particulate elemental selenium.

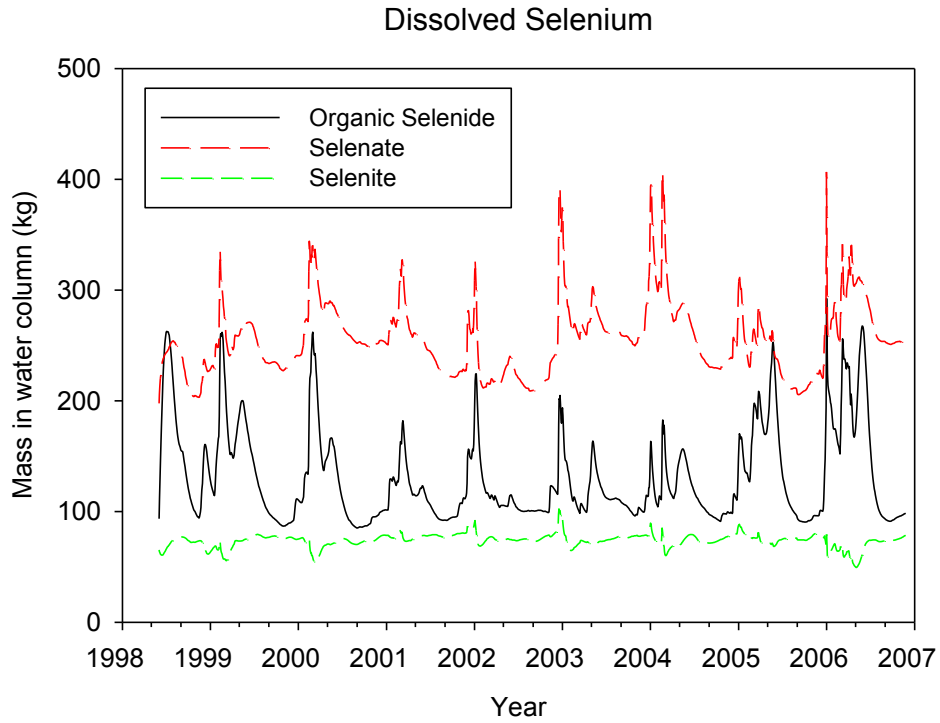


Figure 4-34 Model simulated standing stock of dissolved selenium for the period of 1999-2006

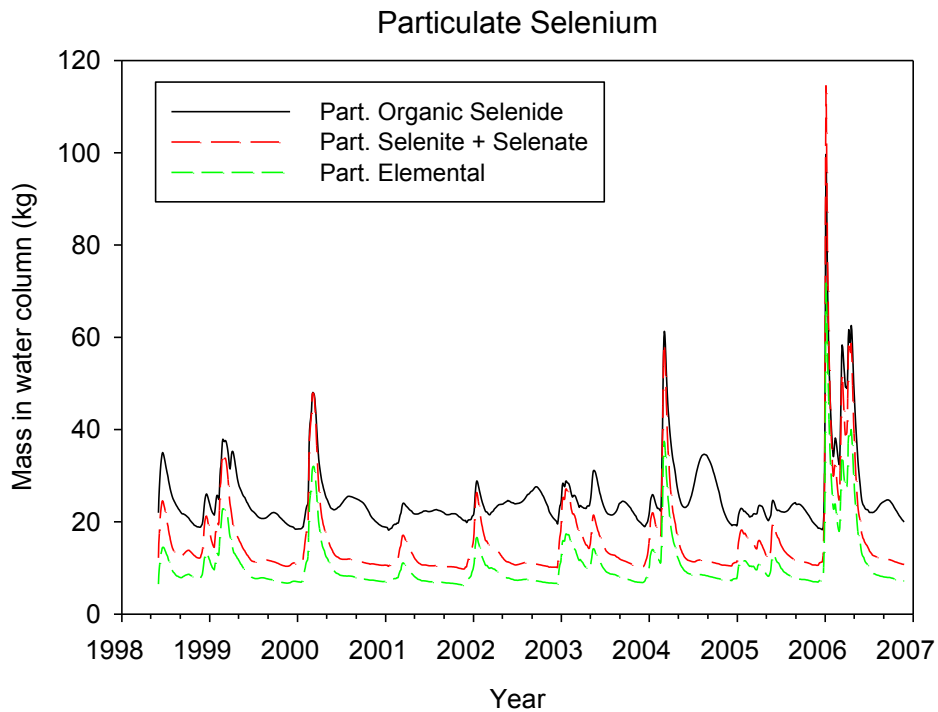


Figure 4-35 Model simulated standing stock of particulate selenium for the period of 1999-2006

Dissolved and particulate selenium undergo a series of transformations. Simulated transformations include phytoplankton uptake of selenite, selenate and organic selenide, mineralization of particulate organic selenide, and oxidation of dissolved organic selenide to selenite and selenite to selenate. The model simulated time series selenium transformation fluxes are shown in Figure 4-36. The oxidation of organic selenide to selenite is a relatively fast process and is the largest transformation flux simulated (0.4–1.1 kg/day). Mineralization of particulate organic selenide (BEPS, PSP, and phytoplankton associated) and the uptake of different species of dissolved selenium by phytoplankton are the second largest fluxes simulated (0.1-0.4 kg/day). Simulated selenium uptake fluxes by phytoplankton are higher during low flow. Adsorption and desorption is at a less significant level. Selenite oxidation is a much slower process and therefore simulated flux of selenite oxidation is at a much lower process.

Model simulated transformation fluxes on an annual basis for the simulation period of 1999-2006 are also shown in the bar diagram (Figure 4-37). Simulated mineralization of particulate selenium for the whole estuary is at rate of approximately 50 kg/yr. Selenium uptake by phytoplankton is at a rate of 50-120 kg/yr. Uptake of selenium by phytoplankton is about the same order of magnitude, although slightly higher than, mineralization of particulate organic selenium. Oxidation of organic selenide, Se(-II), to selenite, Se(IV) is at 150-250 kg/yr. Selenite oxidation to selenate, Se(VI), is negligible.

The mass balance plots presented in this section provide an error check, in that there is no loss or creation of mass, an essential test for a numerical model. The summary information on individual processes can be used to determine their relative significance, and better target future data collection as discussed in a subsequent section.

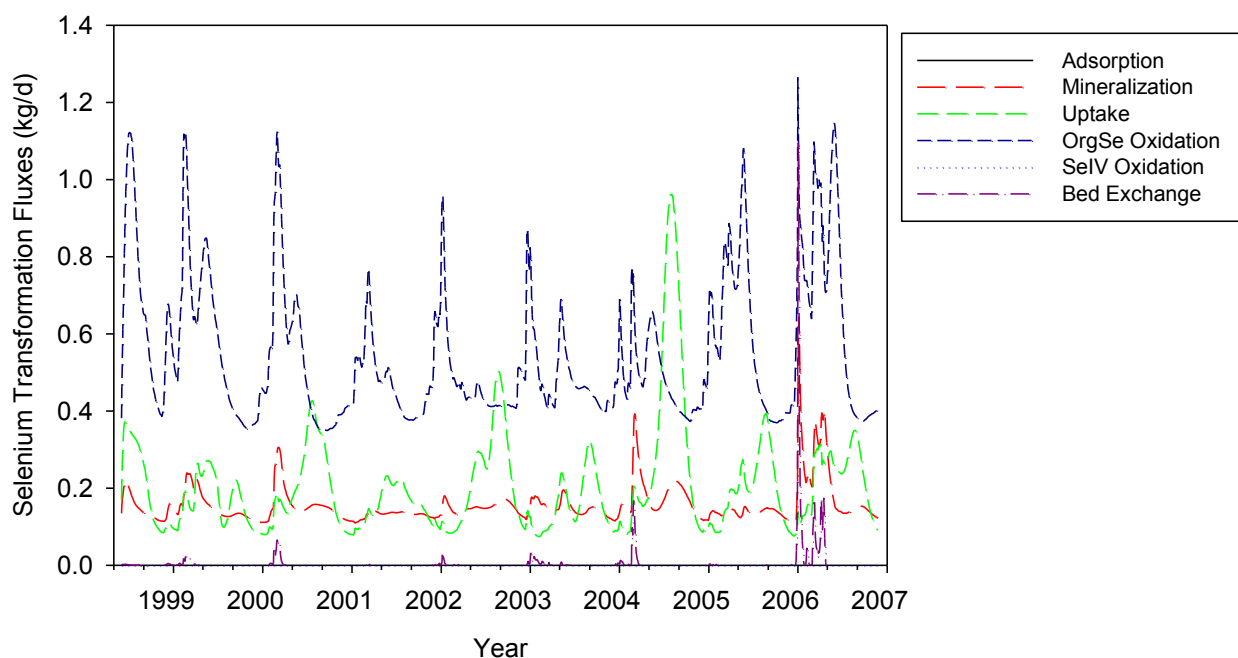


Figure 4-36 Model simulated selenium transformation for the period of 1999-2006

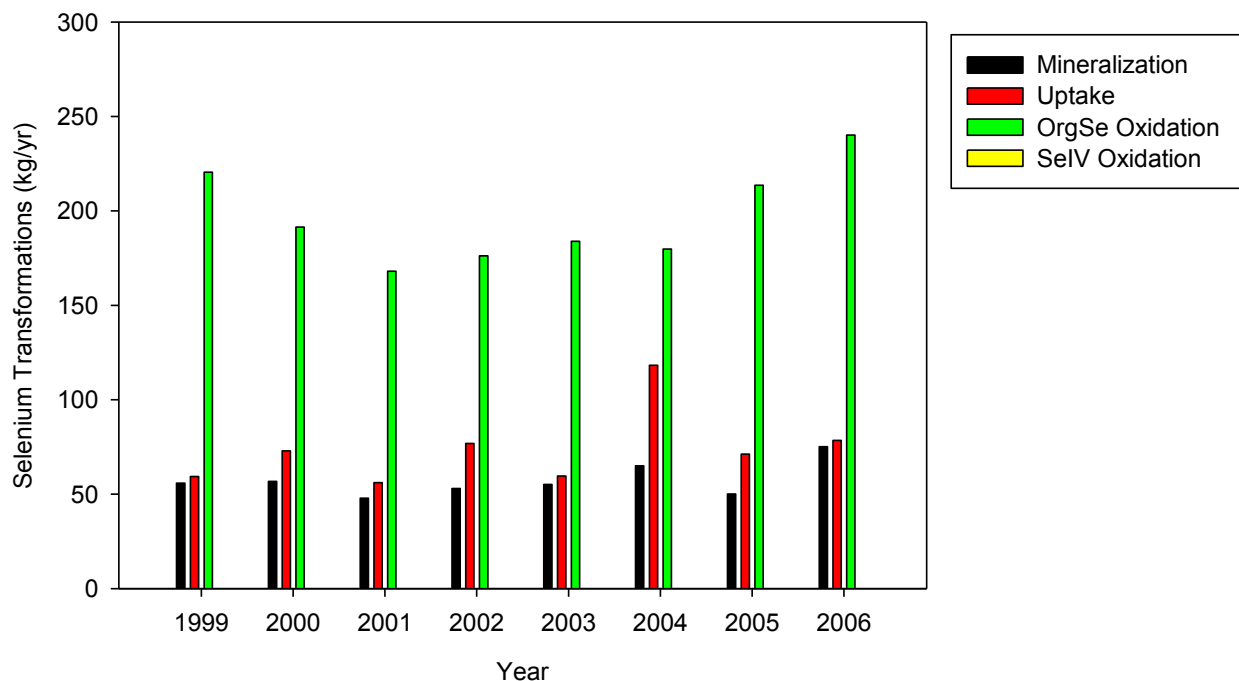


Figure 4-37 Model simulated selenium transformations for the period of 1999-2006

4.7. IMPACTS OF DOMINANT PHYTOPLANKTON SPECIES

Due to the variation of phytoplankton species through time and location in the estuary and large variations in selenium content associated with different phytoplankton species (Lehman, 2001; Baines et al. 2004), particulate selenium concentrations in the estuary may show large variation due to changes in phytoplankton species. Selenium concentrations in phytoplankton generally follow the order of golden brown algae > dinoflagellates > diatoms > green algae. Model simulations were conducted by assuming one dominant species of phytoplankton for each scenario to evaluate the impacts of phytoplankton species on particulate selenium.

The four scenarios include dominant species by golden brown algae (Se:C: 30.62 $\mu\text{g/g}$), diatom (*Chaetoceros gracilis*; Se:C 2.34 $\mu\text{g/g}$), green algae (0.248 $\mu\text{g/g}$) and diatom (*Skeletonema costatum*; 0.004 $\mu\text{g/g}$), with reported selenium content varying by several orders of magnitude among species. The predicted Se:C ratios are shown in Figure 4-38.

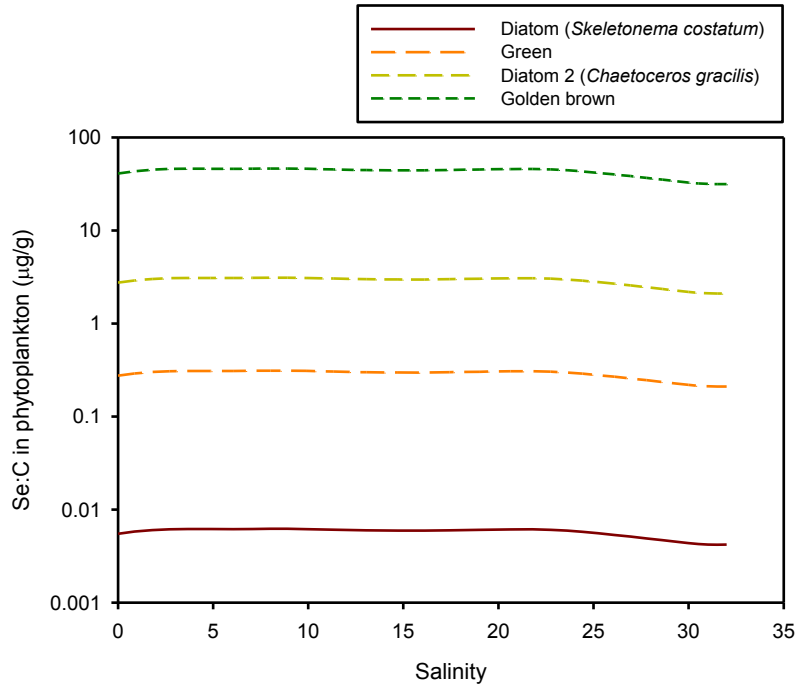


Figure 4-38 Simulated Se:C in phytoplankton by assuming different dominant phytoplankton species in the estuary

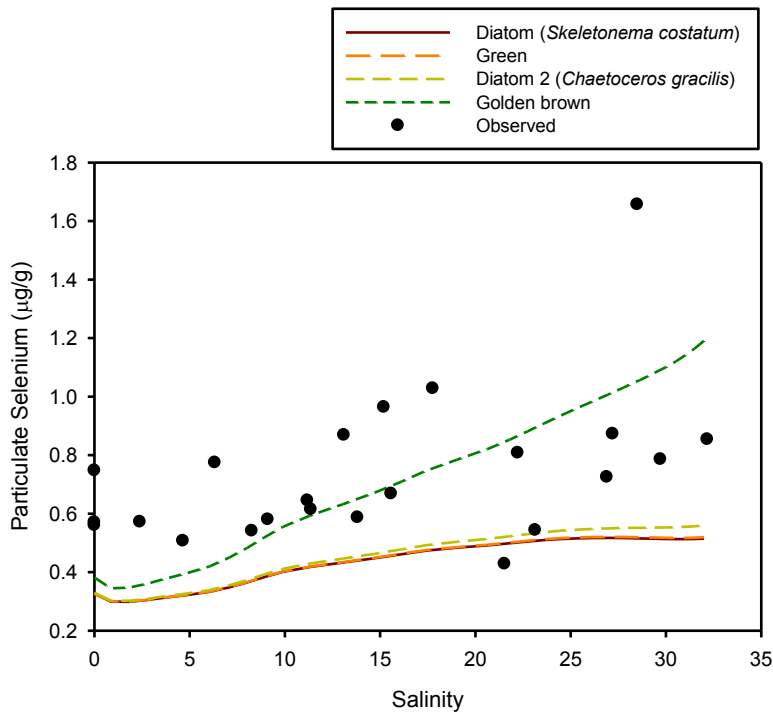


Figure 4-39 Simulated particulate selenium concentrations (in µg/g) by assuming different dominant phytoplankton species in the estuary

Simulated particulate selenium concentrations for golden brown algae are higher than other species and are more comparable with observed particulate selenium concentrations (Figure

4-39). Simulated selenium concentrations in bivalves also show a factor of 2-3 difference by different phytoplankton species. Particularly the golden brown algae resulted in significantly higher selenium concentrations in bivalves (Figure 4-40). In summary, if phytoplankton species shift from golden brown to green algae, lower selenium concentrations in particulates and bivalves and slower response in particulate selenium to load changes are expected.

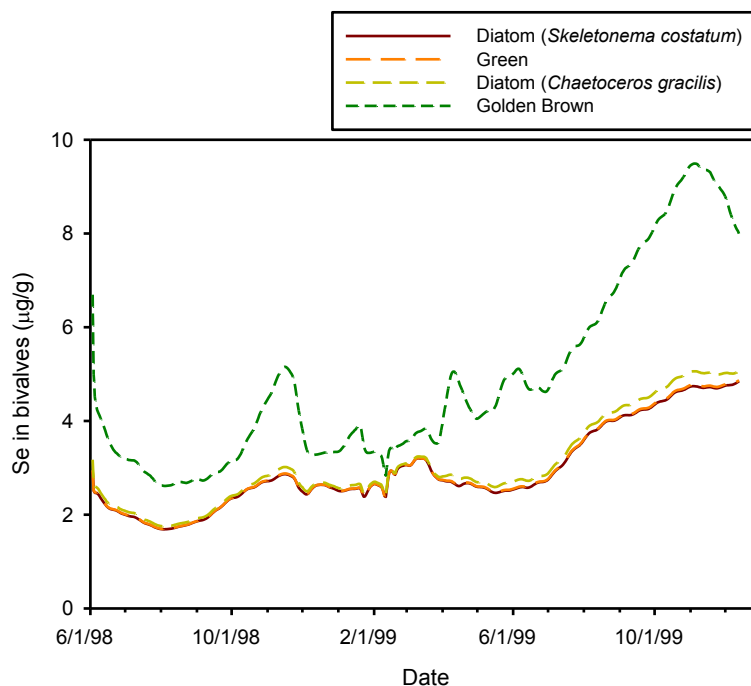


Figure 4-40 Simulated selenium concentrations in bivalves by assuming different dominant phytoplankton species.

4.8. COMPARISON WITH SPATIAL TRENDS IN PARTICULATE SELENIUM OBSERVATIONS

Particulate selenium in the estuary during low flows shows a small increasing trend with salinity. The increase appears to correspond with increases in chlorophyll a and pheophytin concentrations (Figure 4-41). The levels of chlorophyll a and pheophytin seem to decrease slightly at salinity 20 and then increase towards seaward boundary. The fraction of phytoplankton (in terms of biomass) in TSM increases with salinity (Figure 4-41, lower panel). Because phytoplankton concentrates selenium to a higher level than mineral particles, the increases in phytoplankton fraction in TSM can contribute to the elevated particulate selenium concentrations near the mouth of the estuary. As a result, particulate selenium concentrations show a positive correlation with fraction of phytoplankton in TSM (Figure 4-42). Even with selenium content in phytoplankton remaining constant through the estuary, the increases in phytoplankton fraction in TSM is able to explain a large portion of the increase in particulate selenium along the estuary.

For chlorophyll a, the high concentrations at the seawater end member are most likely due to both in situ production and advection from seawater. However it is difficult to differentiate from the measurements which process dominates. In the model, a seawater endmember concentration of 2.3 µg/L is specified for chlorophyll a.

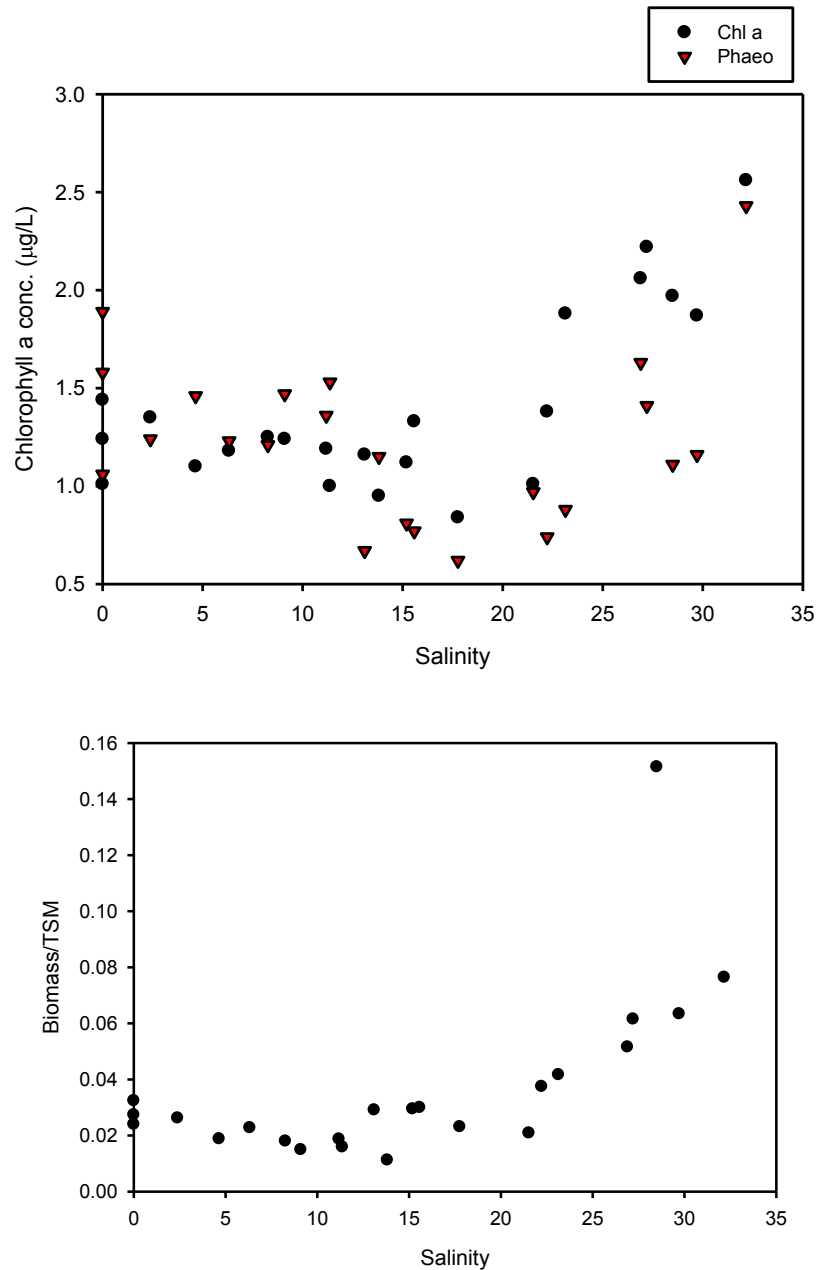


Figure 4-41 (a) Chlorophyll a (Chl a) and phaeophytin (Phaeo) concentrations and phytoplankton as a function of salinity. Phaeophytin is a degradation product of chlorophyll a and these concentrations are indicative of live and senescent algal biomass. (b) Biomass as a fraction of TSM over the salinity gradient. Data are for a low flow period (November, 1999), and show the increase in algal suspended biomass (live and dead algae) and increasing proportion of biomass in suspended particulates along the salinity gradient.

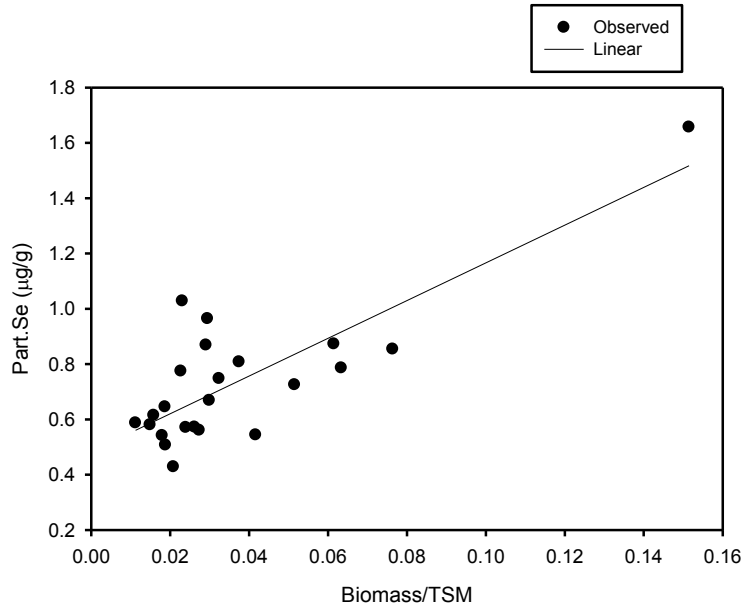


Figure 4-42 Correlation between particulate selenium concentrations and phytoplankton biomass as fraction in TSM (Source: Doblin et al. 2006).

The model-predicted slow changes in particulate selenium concentrations due to changes in dissolved selenium concentrations seem to agree with observed patterns in Doblin et al. (2006). Particulate selenium concentrations for September 1986 seem to be similar to observed concentrations in October 1998 and November 1999 (Figure 4-43), while for this time period refinery loads decreased by 3.85 kg/day and selenite concentrations show a 47% decrease (Figure 4-44).

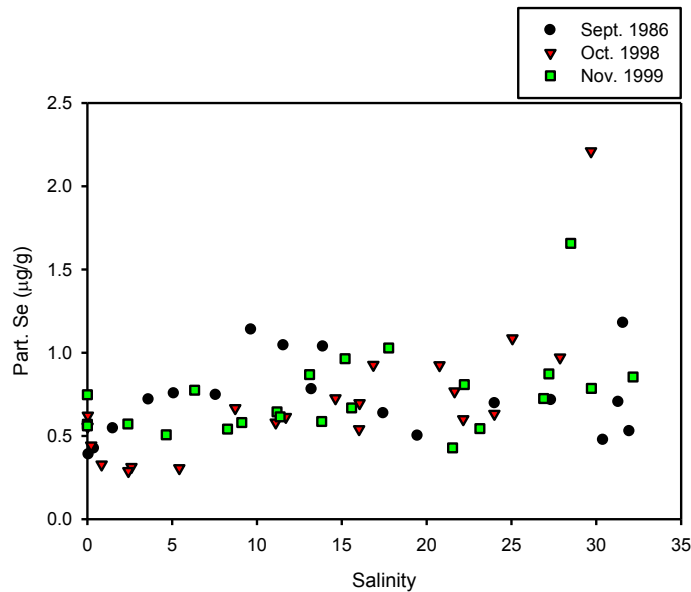


Figure 4-43 Particulate selenium concentrations (in µg/g) under low flow for September 1986, October 1998 and November 1999 (source: Doblin et al. 2006).

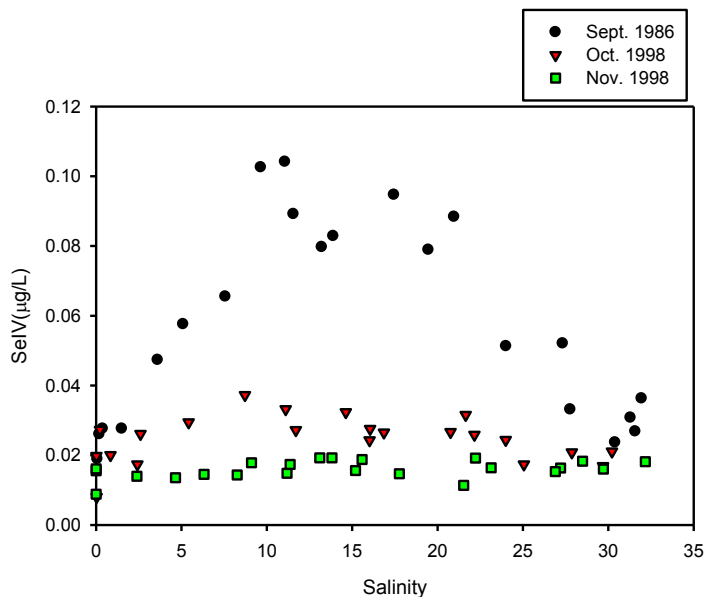


Figure 4-44 Selenite concentrations (in µg/L) under low flow for September 1986, October 1998 and November 1999 (Source: Doblin et al. 2006).

4.9. SUMMARY OF EXPANDED MODEL TESTING

The additional model evaluation presented in Section 4, combined with evaluation of the model against data that were not used for calibration (Section 3), provides confidence in the model formulation, parameterization, and input loads used in this work. The following key features from the modeling work are significant:

- The model is able to capture variation in the dissolved and particulate selenium data, including data at the species level. Not every feature of the observed data are fit, but across a range of dates and hydrologic conditions, the model is able to reproduce average conditions reasonably well. The model also represents average conditions in TSM and chlorophyll a well, although it does not do as well at matching peaks in space and time.
- The model is able to represent ranges of biological selenium data, including data in bivalves and predator species. For bivalves, the model represents seasonal ranges of concentrations well.
- A model hindcast, applied to 1986 conditions, when refinery and San Joaquin River loads were higher than present, performed very well in matching the dissolved and particulate selenium concentrations.
- The model is run using riverine input loads over 1999-2006 that are constructed from data collected in 1999. Even with this simplification, the model is able to represent various features of the annual and seasonal trends in bivalve data, especially when a range of boundary values are used to run the model.

5. MODEL PREDICTIONS

The preceding steps of model calibration and evaluation against new data (Section 3) and testing under an expanded range of conditions (Section 4), set the stage for us to present scenarios where predictions of selenium concentrations in various compartments (dissolved, particulate, sediments, bivalves) are made under imposed load changes. As this TM is being prepared, numeric targets for the TMDL are still not final, and the load scenarios presented in this section are not meant to imply a specific load allocation for the TMDL, but primarily to summarize our understanding of the linkage between sources and various endpoints of interest as embodied in the model. A test is also performed allowing for a consistent increase in San Joaquin River flows to the Delta, to describe a future condition where Delta exports preferentially withdraw Sacramento River water. Finally, for further evaluation of these results, the model predictions for a selected load change scenario are compared against predictions made using the Presser and Luoma (2006) approach.

5.1. LOAD CHANGE SCENARIOS

A series of load-change scenarios were run to evaluate the effects of changing point and non-point sources on the dissolved and particulate selenium concentrations in water and selenium concentrations in bivalves. These scenarios are listed in Table 5-1, and represent scenarios that are within the range of plausibility (e.g., 30-50% reductions) to those that are extreme (such as complete removal of all tributary and point source loads). The goal is to demonstrate the model response under a wide range of conditions.

For performing the model prediction simulations, clam ingestion rates and assimilation efficiencies of different selenium particulate species by bivalves are listed in Table 5-2.

For each scenario, the model provides predictions for all dissolved and particulate species in time and space, as well as concentrations in biota. These calculations are performed over 1999-2006, and, as noted in Section 4, use two sets of particulate boundary conditions, for the riverine and seawater ends, to provide an estimate of the future range of conditions. Example results are shown comparing the base case results to Scenario 2 in Figure 5-1. In this case, the spatial distribution of dissolved selenium and particulate selenium is shown, where each is computed by summing the species-level data. These plots show the response of the dissolved concentration to the change in dissolved load, and the minimal response in particulate concentrations. Also shown in the plots is the response of the particulate concentrations to using different particulate boundary conditions. The particulate boundary conditions have minimal impact on the dissolved concentrations. Temporal results from the base case and Scenario 2 are shown in Figure 5-2 for a specific location in the estuary (Carquinez Strait). The temporal results are consistent with spatial results, in that Scenario 2 results in a change in dissolved-phase concentrations although not in the particulate or bivalve concentrations.

**Table 5-1
Load Change Scenarios Tested Using the Model**

Scenario	Description	Loading Factors as a Fraction of Base Case Loads, Unless Specified as a Concentration in $\mu\text{g/l}^5$							
		Riverine Particulate Selenium Loads			Dissolved Selenium Loads				
		BEPS	PSP	Phyto	Sac.	SJR.	Ref.	Trib.	POTWs
1	Base case	1	1	1	1	1	1	1	1
2	Removal of all point source loads (refineries, POTWs), and local tributary loads	1	1	1	1	1	0	0	0
3	30% reduction in refinery and San Joaquin River loads, dissolved only	1	1	1	1	0.7	0.7	1	1
4	50% reduction in all point sources (refineries, POTWs), local tributaries and San Joaquin River loads, dissolved only	1	1	1	1	0.5	0.5	0.5	0.5
5	Increase dissolved selenium loads from San Joaquin River by a factor of 3, particulate loads remain the same as the base case	1	1	1	1	3	1	1	1
6	Decrease dissolved selenium loads from San Joaquin River by a factor of 50%, particulate loads remain the same as the base case	1	1	1	1	0.5	1	1	1
7	Increase particulate selenium loads associated with PSP, BEPS, and phytoplankton from Sacramento River by a factor of 3, dissolved loads remain the same as the base case	3	3	3	1	1	1	1	1
8	Decrease particulate selenium loads associated with PSP, BEPS, and phytoplankton from Sacramento River by a factor of 50%, dissolved loads remain the same as the base case	0.5	0.5	0.5	1	1	1	1	1
9	Increase San Joaquin River particulate loads by 3x, other loads stay the same	1	1	1	1	1	1	1	1
10	A natural load scenario, where the point sources are zero, the local tributary loads and speciation are at Sacramento River values, and the San Joaquin River is at 0.2 $\mu\text{g/l}$, at current speciation	1	1	1	1	0.2 $\mu\text{g/l}$	0	Sac. R. levels	0

⁵ Base case loads are not constant through time in the simulations. When a load change is imposed, this means that the entire time series of load inputs is multiplied by the same factor.

Table 5-2
Parameters for DYMBAM Model Used in Model Prediction Simulations

No.	IR, g/g/day	AE (particulate elemental selenium, PSe0), fraction	AE (particulate adsorbed selenite and selenate, PSeivvi), fraction	AE(particulate organic selenide, POrgSe), fraction
1	0.65	0.2	0.45	0.8

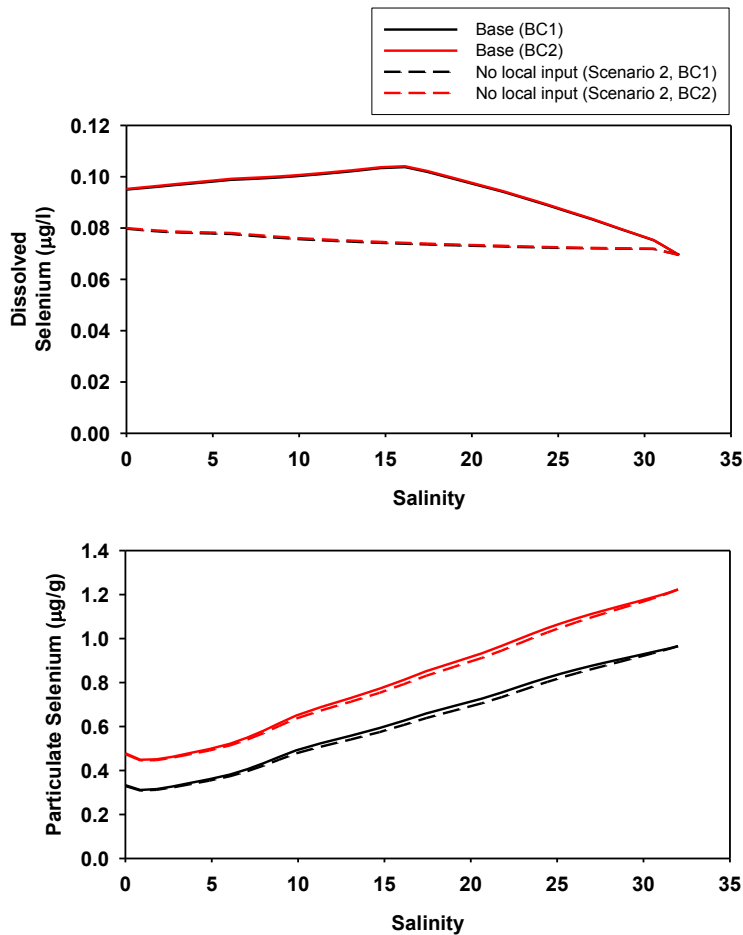


Figure 5-1 Comparison of base case results with Scenario 2 (no local point source or tributary inputs) for a simulated date of November 11, 1999. Results are shown for dissolved selenium (sum of selenate, selenite, and organic selenide), and particulate selenium (elemental selenium, organic selenide, and adsorbed selenate+selenite). BC1 and BC 2 refer to the higher and lower boundary conditions associated with particulates presented in Section 4. For Scenario 2, the change in loads results in a significant change in dissolved concentrations, which are insensitive to the boundary condition used. Particulate and bivalve concentrations, in contrast, although dependent on the boundary condition used, show no change in Scenario 2.

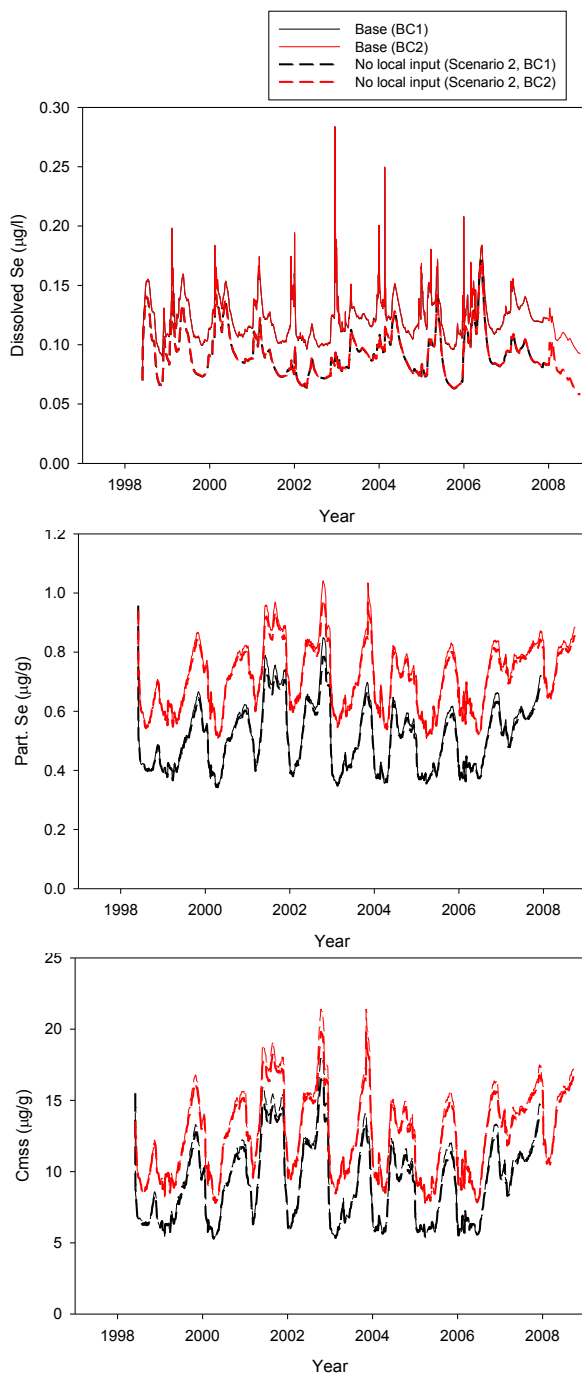


Figure 5-2 Comparison of base case results with Scenario 2 for Carquinez Strait over 1999-2006. Results are shown for dissolved selenium (sum of selenate, selenite, and organic selenide), and particulate selenium (elemental selenium, organic selenide, and adsorbed selenate+selenite), and bivalves. BC1 and BC 2 refer to the higher and lower boundary conditions associated with particulates. As seen in the previous figure, for Scenario 2, the change in loads results in a significant change in dissolved concentrations, which are insensitive to the boundary condition used. Particulate and bivalve concentrations, in contrast, although dependent on the boundary condition used, show no change in Scenario 2.

To present the results of the base case plus the nine scenario cases in Table 5-1 (ten scenarios in all), a more compact presentation is used as shown in Figure 5-3, Figure 5-4, and Figure 5-5. These box plots allow side-by-side comparison of scenario results, along with consideration of the two particulate boundary conditions for each scenario. The range of values associated with specific months in the simulation period, representing a wet and a dry year are shown, including the variability computed by the model for the selected month. As in the previous figures, the constituents shown are dissolved selenium (all species), particulate selenium (all species), and bivalve selenium. Data are shown for April 1999 (wet month in a wet year), November 1999 (dry month in a wet year), and July 2001 (dry month in a dry year). The last period represents a condition where selenium uptake and bioaccumulation may be exacerbated due to long residence times.

The following observations can be drawn from the set of scenarios presented here:

- Certain loads, including point sources and local tributary contributions, are considered to be entirely in the dissolved form. When these loads are reduced (Scenarios 2, 3, and 4), there are corresponding decreases in the dissolved concentrations, but minimal change in particulate species concentrations. The overall decrease is nonetheless limited, because the Sacramento River dissolved load, a large, low concentration flow, is not decreased in any scenario.
- The additional variability imposed by using two boundary conditions for particulates is clearly visible in the concentrations calculated for bivalves and particulates.
- Changes in the bivalve concentrations of selenium (expressed as $\mu\text{g/g}$) follow trends in particulate concentrations, with lower values during a high flow month, and higher values during a low flow month.
- Scenario 5, a tripling of the San Joaquin River dissolved load, has a major impact on dissolved phase concentrations, and a smaller, although still significant, impact on the particulate concentrations.
- Scenario 6, a 50% decrease of the San Joaquin River dissolved load shows limited impact on dissolved and particulate concentrations, in large part because the decrease is swamped by the contribution of the Sacramento River load.
- Scenarios 7 and 8, tripling and a halving of the Sacramento River particulate load only (the dissolved load is unchanged), show a major effect on the particulate and bivalve concentrations (an increase and a decrease respectively).
- Scenario 9, a tripling of the San Joaquin particulate selenium load, with all dissolved loads remaining unchanged, results in an increase in the bay particulate and bivalve concentrations, albeit not as large as change as caused by an increase in the Sacramento River particulate concentrations (Scenario 7).
- Scenario 10, using what might be natural selenium loads in the system, shows a major impact on the dissolved phase concentrations, and a smaller effect on the particulate and bivalve concentrations.
- The overall sensitivity of the estuary to load changes from local tributaries and point sources is greater during dry months, especially during a dry year. This relates to the

lower contribution from the Delta in these periods and the longer residence time in the bay.

Overall, these scenarios provide insight into the representation of the bay in the ECoS model framework, and highlight most important sources that relate to endpoints of interest in the TMDL. They demonstrate the somewhat different behavior of dissolved and particulate selenium over time scales and residence times that pertain to the simulation period, even though it is known that the two phases are inter-related through uptake, mineralization, and adsorption/desorption.

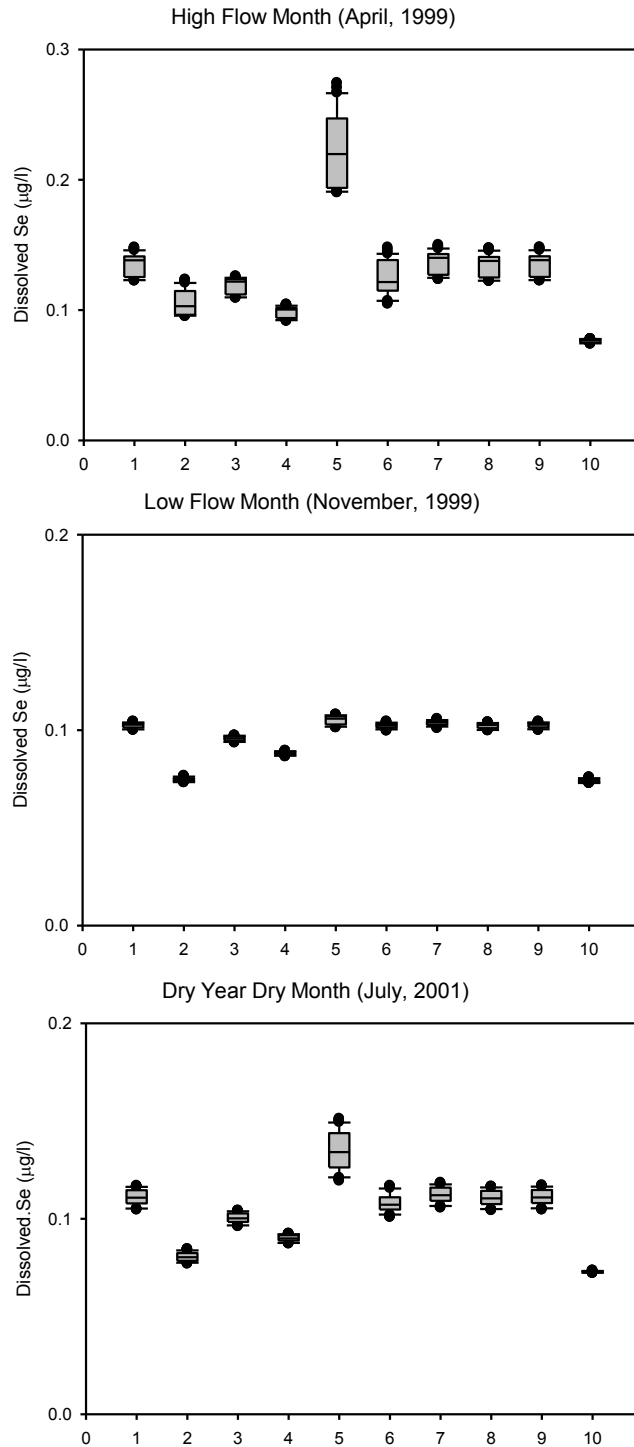


Figure 5-3 Impacts of Scenarios 1-10 on dissolved selenium concentrations for three months of the simulation period, representing a wet year (1999), and a dry year (2001). The periods shown include a wet month (April 1999), and two dry months (November 1999 and July 2001). The response due to each loading scenario varies by season. Simulated concentrations for Carquinez Strait are compared.

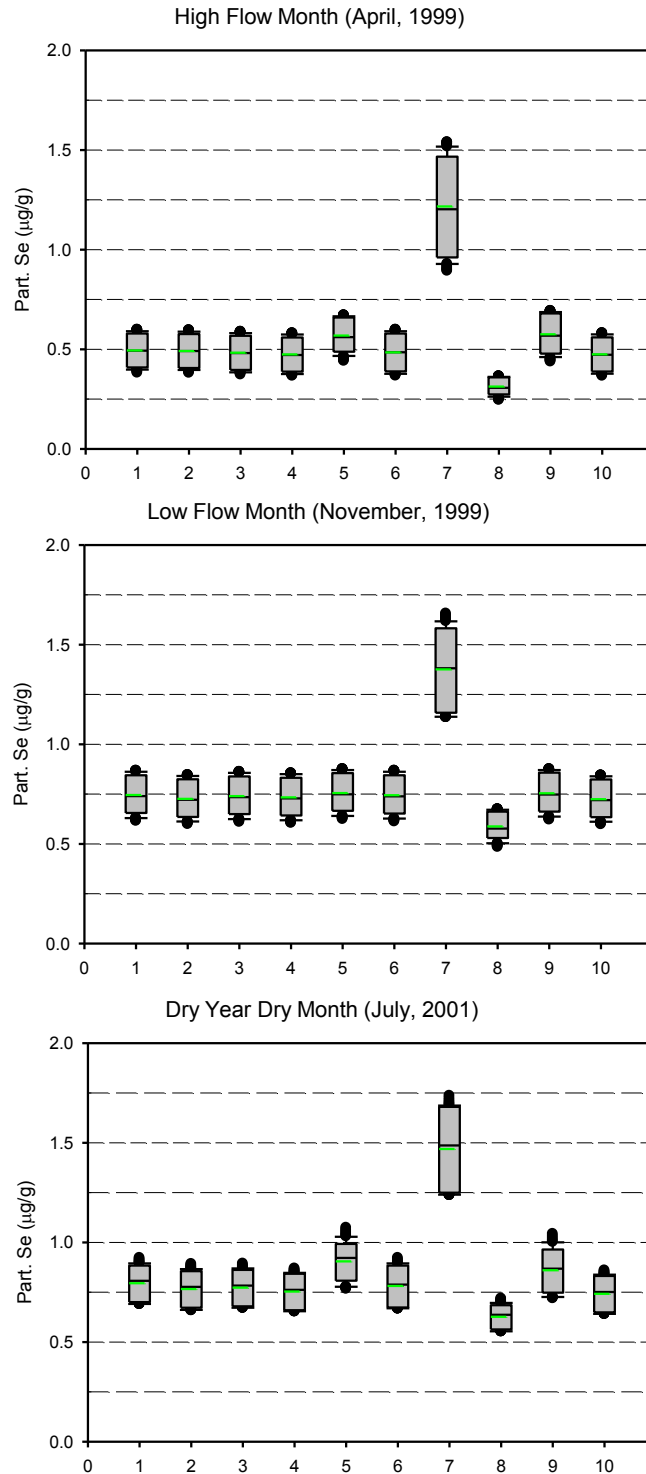


Figure 5-4 Impacts of Scenarios 1-10 on particulate selenium concentrations for three months of the simulation period, representing a wet year (1999), and a dry year (2001). The periods shown include a wet month (April 1999), and two dry months (November 1999 and July 2001). The response due to each loading scenario varies seasonally, and also shows different behavior from dissolved selenium concentrations, especially Scenarios 5, 7, and 10. Simulated concentrations for Carquinez Strait are compared.

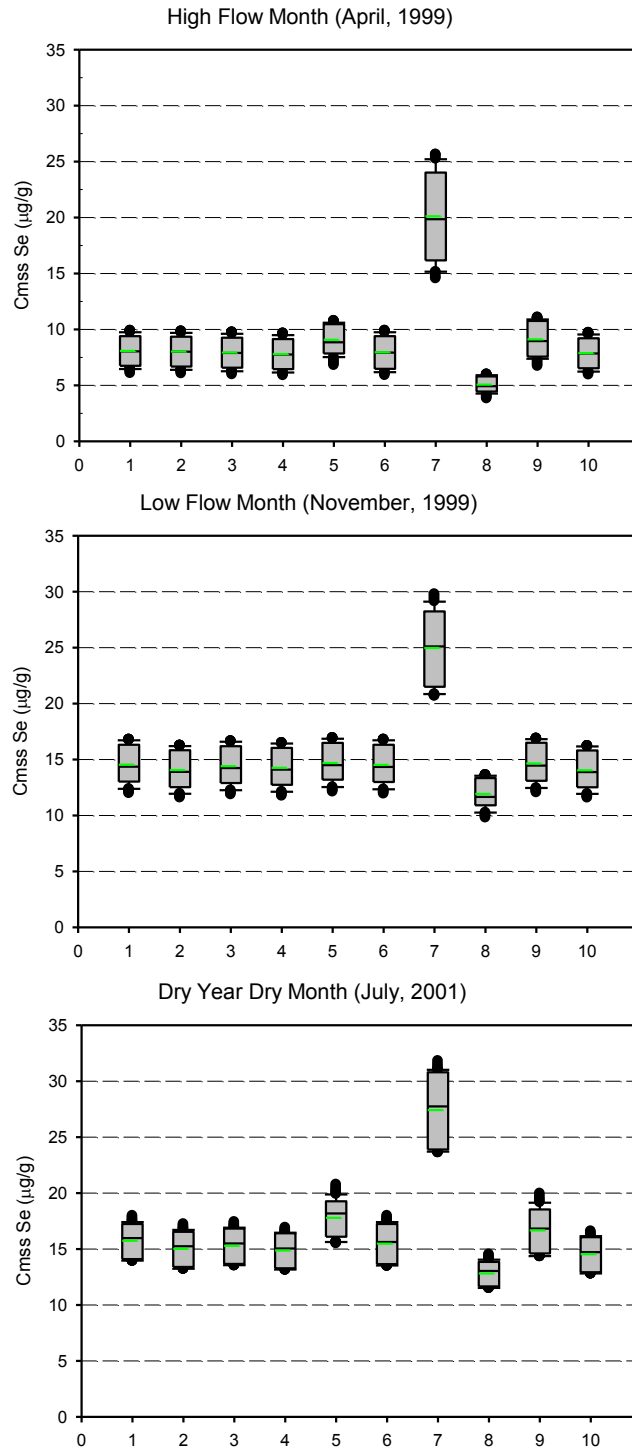


Figure 5-5 Impacts of Scenarios 1-10 on bivalve selenium concentrations for three months of the simulation period, representing a wet year (1999), and a dry year (2001) for the same seasons as shown in the prior two figures. The response due to each loading scenario varies seasonally, and is correlated with the particulate concentrations. Concentrations are systematically higher during the two dry months shown, and higher concentrations occur in the dry month of a dry year. Simulated concentrations for Carquinez Strait are compared.

5.2. EFFECTS OF INCREASING SAN JOAQUIN RIVER FLOW

To test the changes in particulate selenium as a result of load changes from the rivers, particularly from the San Joaquin River, the model was run using the same scenario as in Meseck (2002), assuming that all the San Joaquin River flow at Vernalis will reach the Bay. This is in contrast with current conditions, where a significant part of the San Joaquin flow is withdrawn from the Delta into aqueducts. Under the elevated flow condition, the Delta removal effect of selenium was also considered to be lost. Therefore, the scenario assumes elevated inputs of selenium as a result of both increase in flow from the San Joaquin River and the loss of delta removal effects on selenium.

Model simulations using San Joaquin River flow at Vernalis were compared to simulation results using normal San Joaquin River flow (base case). Under the base case, flow from the San Joaquin River was estimated as the difference between Delta outflow and flow from the Sacramento River at Rio Vista. Simulated dissolved and particulate selenium concentrations were higher under the scenario of increased San Joaquin River flow than the base case, for both high flow and low flow periods (Figure 5-6 and Figure 5-7).

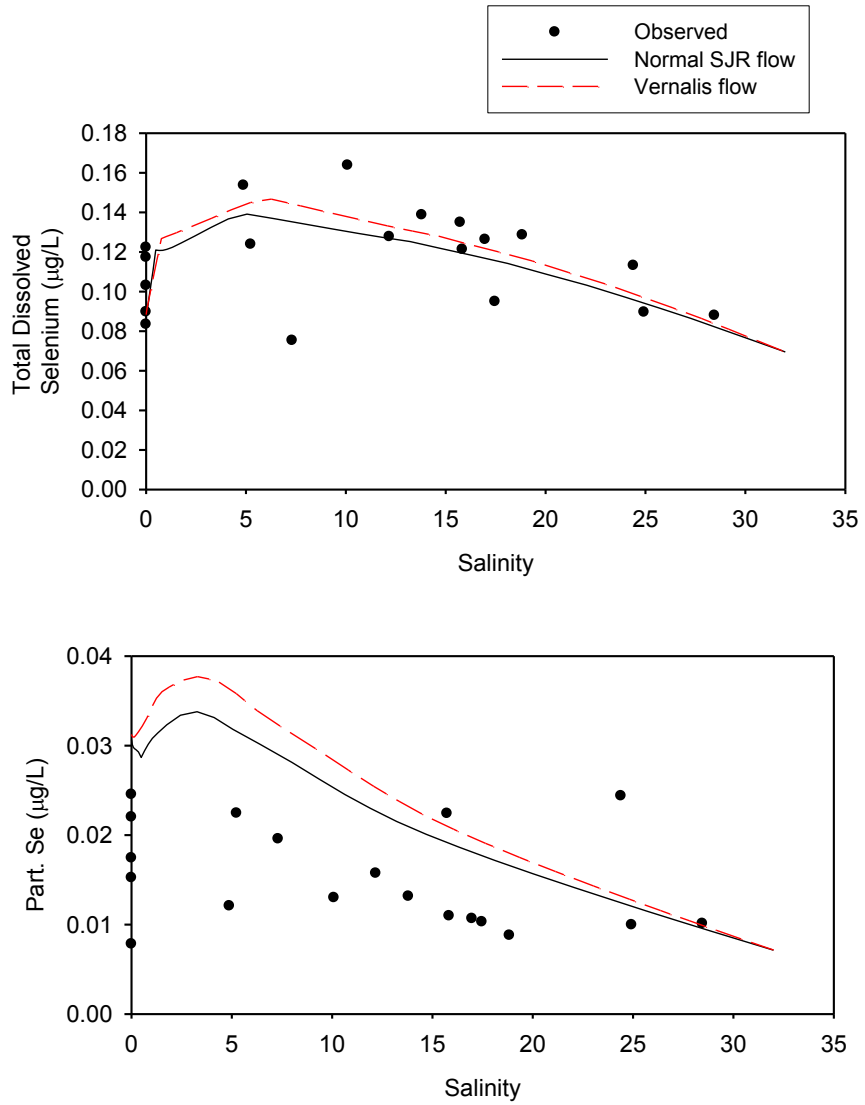


Figure 5-6 Predicted dissolved and particulate selenium for different San Joaquin River discharge during a high flow period (April 14, 1999).

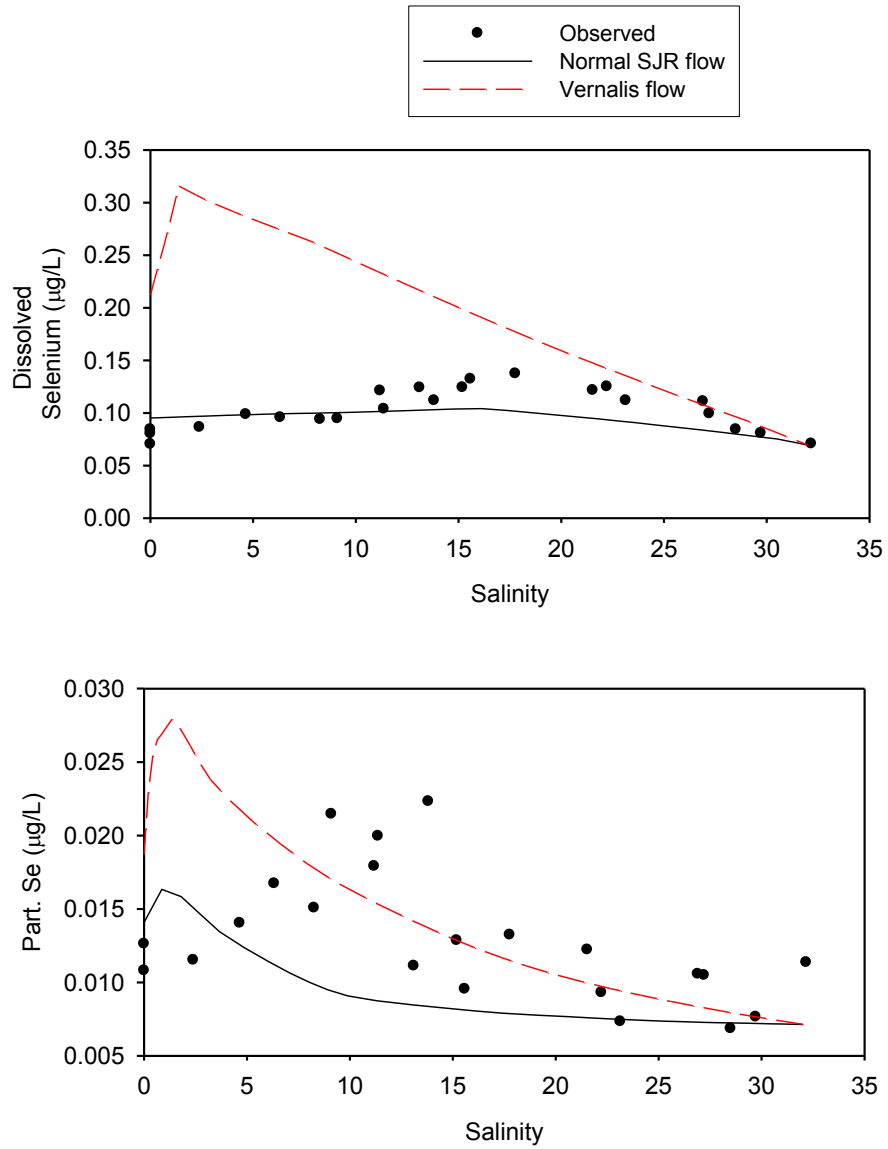


Figure 5-7 Predicted dissolved and particulate selenium for different San Joaquin River discharge during a low flow period (November 11, 1999).

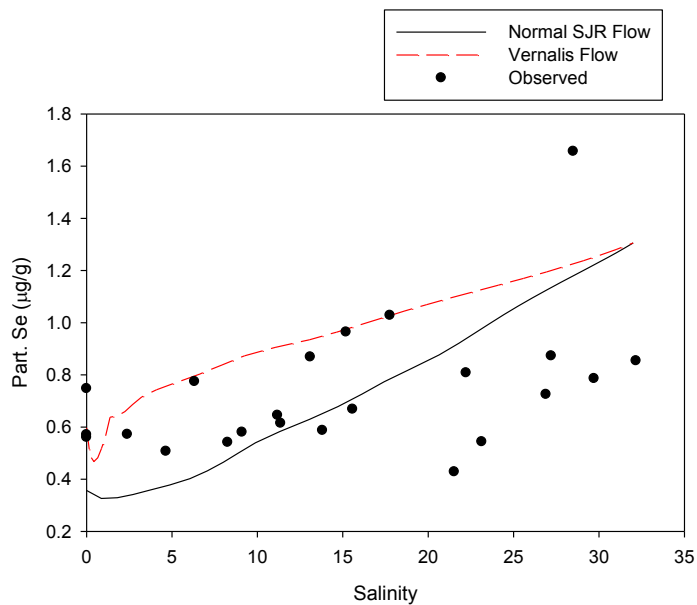


Figure 5-8 Predicted particulate selenium concentration ($\mu\text{g/g}$) under estimated San Joaquin River flow at the confluence compared to the prediction for flow at the confluence set to the Vernalis flow rate.

Predicted model-simulated selenium concentrations on particulates ($\mu\text{g/g}$) are significantly higher under the scenario of increased San Joaquin River flow, particularly for the upper estuary. Setting the flow of the San Joaquin River to the measured flow at Vernalis, particulate selenium concentrations are nearly doubled with increases greater than $0.4 \mu\text{g/g}$ predicted in the upper estuary (Figure 5-8).

5.3. COMPARISONS WITH THE PRESSER AND LUOMA (2006) APPROACH

As discussed in more detail in TM-5, the Presser and Luoma model conceptualizes the fate of selenium under various loading scenarios, with an emphasis on sources from the Central Valley, including the San Joaquin River, the Sacramento River, and from petroleum refineries. Concentrations at the head of the estuary are estimated as the flow-weighted average of all influent concentrations as shown in Figure 5-9. Concentrations at Carquinez Strait are half of these values, based on sea-water mixing. Particulate concentrations are estimated using a range of K_d values appropriately chosen for different aquatic environments (1,000, 3,000, and 10,000 L/Kg).

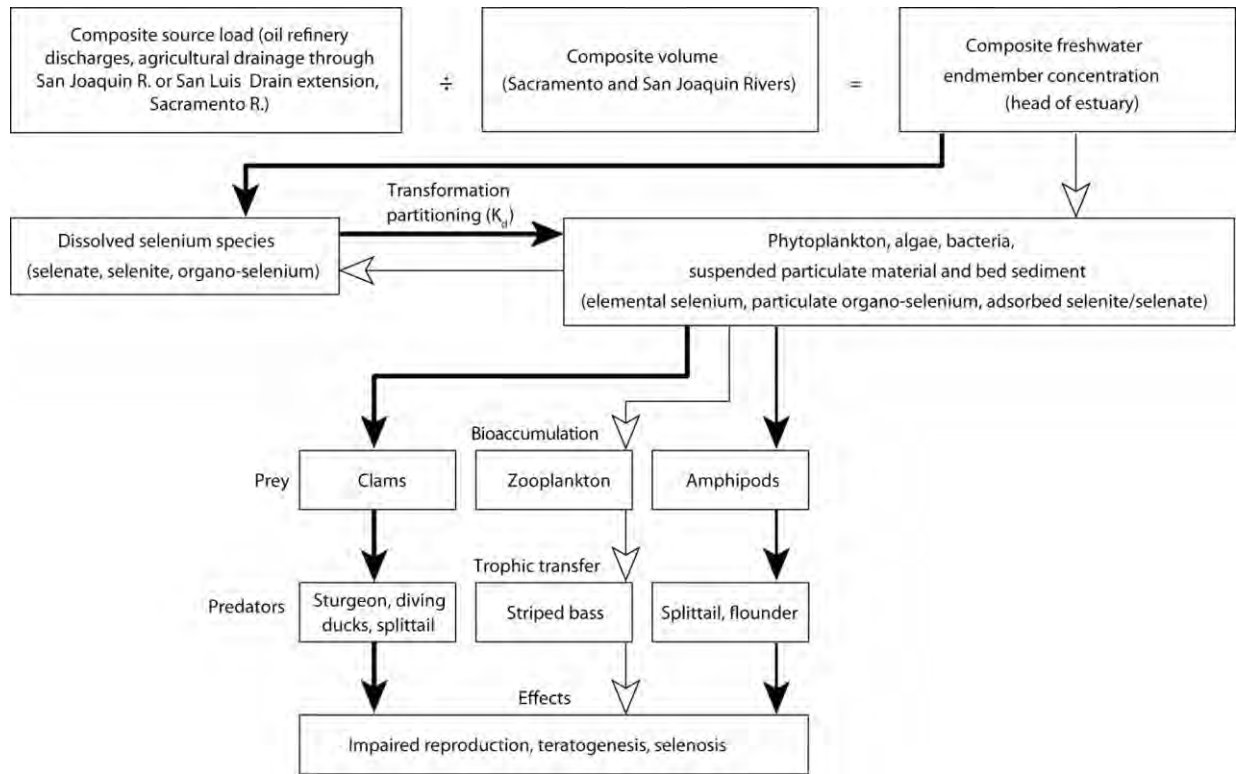


Figure 5-9 Conceptual model describing linked factors that determine the effects of selenium on ecosystems. (from Presser and Luoma, 2006)

Using flow values for different hydrologic periods, this approach can be used to calculate selenium concentrations at the head of the estuary and in Carquinez Strait. An example calculation, building on a wet year, low flow season scenario presented in Presser and Luoma (2006), is shown in Figure 5-10. For this specific scenario, loading from the proposed San Luis Drain was set at zero in the original work.

Source	Flow (million acre-feet)	Se Conc (ug/L)
Sacramento River	2.3	0.04
San Joaquin River	0.5	2.5
Refineries	0.005	50
Selenium concentrations		
Head of the estuary	0.57 ug/L	
Carquinez Strait	0.28 ug/L	
Particulate Selenium		
Kd = 1,000 L/kg	0.57 ug/g	
Kd = 3,000 L/kg	1.70 ug/g	
Kd = 10,000 L/kg	5.68 ug/g	

Figure 5-10. Presser and Luoma (2006) calculations of selenium in the NSFB based on flows and concentrations in the Sacramento River, San Joaquin River, and the refineries.

The approach presented by Presser and Luoma (2006) can also be applied to data employed in these calculations, with the change that some additional sources, notably local tributaries and non-refinery point sources, are identified, and updated concentrations for all sources are used. These calculations are shown in Figure 5-11 and are compared with the ECoS-based NSFB model calculations presented earlier (Scenario 4 in Table 5-1, 50% reduction in all loads except Sacramento River). This plot shows significant differences between the two approaches, especially average values calculated, and the range of concentrations across the salinity gradient. Extending the calculations to particulate selenium (Figure 5-12), we can see a critical difference: the Luoma and Presser approach indicates a particulate concentration decrease for the load reduction embodied in Scenario 4, whereas the ECoS-based approach does not. This response is critical in evaluating the use of these models for the TMDL. The linear response in the Presser and Luoma approach may overstate the anticipated response in particulate concentrations to any changes in load.

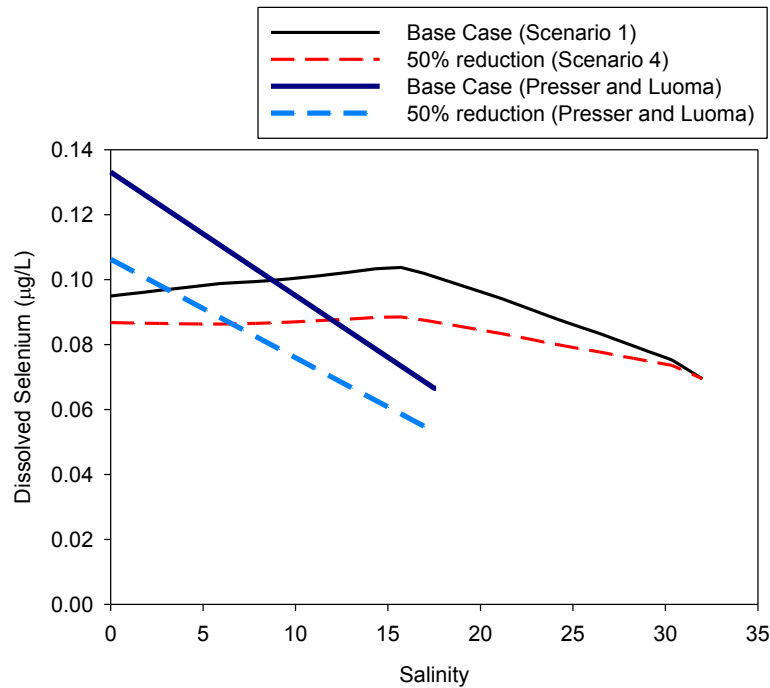


Figure 5-11 ECoS-based model calculations for load reduction Scenario 4 compared with Presser and Luoma (2006) calculations for the same load reduction. The value in the mid-salinity range corresponds to the division by two employed to reflect sea water mixing at Carquinez Strait in the Presser and Luoma approach. The diagonal lines are shown for comparison with the ECoS-based approach; Presser and Luoma (2006) do not report dissolved selenium for all salinities.

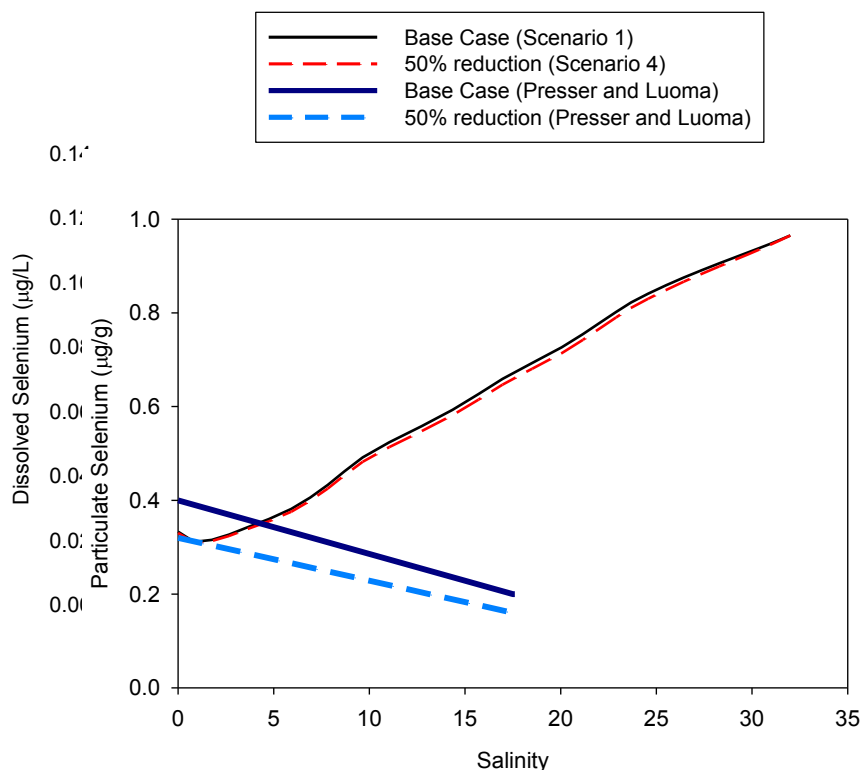


Figure 5-12 Particulate selenium from ECoS model calculations compared with particulate concentrations using the Presser and Luoma (2006) approach with values of K_d set at 3,000 L/kg. The diagonal lines are shown for comparison with the ECoS-based approach; Presser and Luoma (2006) do not report particulate selenium for all salinities.

The comparison of the simple and complex models provides an understanding of the strengths and weaknesses of each approach. The Presser and Luoma (2006) model is easy to explain to stakeholders and is relatively transparent, which are clearly valuable assets in a TMDL-setting process. However, the model does not fully capture the processes associated with particulate selenium uptake, which influence the results obtained for load changes from the base case, a feature that is also of importance to the TMDL.

6. DISCUSSION

The preceding sections have detailed the development and refinement of a model of selenium transport and bioaccumulation in North San Francisco Bay. The model is built on previously published work (Meseck and Cutter, 2006; Presser and Luoma, 2006), and extends it in some important ways that directly relate to the selenium TMDL for the bay. This includes detailed characterization of all point and local tributary sources, use of the most recent data for driving the model, detailed characterization of particulate selenium, and inclusion of uptake/bioaccumulation by filter feeders and predator organisms. Below we discuss the application, calibration, and performance of the model, and the key insights derived from this work.

6.1. MODEL INPUTS

The model was run using input data from a variety of sources, not all of which were measured at the same frequency. Important model inputs for which data were generally available over a simulation period of 1999-2006, include flows in the rivers and local tributaries, chlorophyll a concentrations, suspended solids concentrations, salinity, and total selenium in the rivers and point sources. Data on selenium speciation (in the dissolved phase and in the particulate phase) on selected loads (refineries and riverine sources) were available primarily for 1999. When simulations were performed over 1999-2006, the model inputs, for most part, were based on observed data. However, because selenium speciation data was not available beyond 1999, much of the speciation of the input loads was based on 1999 conditions, i.e., the speciation ratios were applied to measured total selenium data. The model input setup thus required some assumptions that, in future, could be addressed through more targeted data collection as discussed below.

6.2. MODEL PERFORMANCE DURING CALIBRATION (1999)

Model calibration involved the selection of the principal transformation rates that pertain to flow, salinity, sediment transport, phytoplankton growth, and selenium chemistry. Many of these values were based on values reported in the scientific literature, although about half the parameters were estimated by adjusting values to fit observed data. The model was calibrated to data primarily from 1999, for which detailed selenium speciation data in the estuary were available.

For the simulation period, the model is able to simulate key aspects of physical and biological constituents that affect selenium concentrations. The model simulates salinity along the estuary well for different hydrological conditions. The evaluation results for phytoplankton and TSM over short-time periods (during specific sampling events for selected years) and long-term periods for multiple years indicated that the model is able to simulate the general temporal and spatial pattern in TSM and phytoplankton, although specific-day peaks may not match very well. For phytoplankton, a few spring blooms are not captured by the model as the model uses a single light limitation function to simulate growth, which limits phytoplankton growth in spring months. Overall, for ancillary parameters, especially TSM and phytoplankton, the model does better at fitting average concentrations than peak concentrations. To some extent this is a consequence of the 1-D formulation of the model, although local variability in driving parameters cannot be ruled out. However, given the hydrodynamic complexities of San Francisco Bay, the inter-annual

and seasonal variability in hydrology, this one dimensional model produces reasonable results of the ancillary variables for use in computing selenium fate and transport.

The simulated selenium species include dissolved forms such as selenite, selenate and organic selenide and particulate species such as adsorbed selenite and selenate, particulate organic selenide and particulate elemental selenium. The transfer of dissolved selenium to particulate selenium is simulated through kinetic adsorption and phytoplankton uptake, and not through equilibrium partitioning. Uptake of selenium by phytoplankton included kinetic uptake of selenite, organic selenide, and selenate, in decreasing order of importance. The uptake rates used in the model simulations are similar to rates used in Meseck and Cutter (2006). During calibration, the model was able to fit the patterns in concentrations of dissolved selenate and selenite well, although it performed less well for dissolved organic selenide. Similarly, the model was able to fit the particulate selenate plus selenite better than the particulate organic selenide. In general the model was better able to represent the general trends in concentration better than the localized spatial variation. The reasons underlying this behavior are not fully understood and may relate to local variability or to small scale processes that are not captured in the 1-D model.

6.3. MODEL PERFORMANCE DURING 1999-2006

Using the 1999 calibrated values for parameters in the model equations, the model was run by varying other inputs over the period 1999-2006. When run in the predictive mode, the model output could be compared with total selenium, which is the only type of selenium data available for years post-1999. This was matched fairly well, although given the degree of aggregation to arrive at this value, it is recognized to not be a strong test of the model.

However, there are other, longer-term data sets for biota to which the model was also applied. The model was able to capture the annual and seasonal variability in clam (*Corbula amurensis*) concentrations fairly well. Although there is less data for comparison, the model also provided reasonable predictions for predator species such as sturgeon and scaup concentrations.

6.4. MODEL PERFORMANCE DURING HINDCAST (1986)

The model was used in a hindcast mode to test predictions in the mid-1980s, where concentrations in many sources, such as the refineries and the San Joaquin River, were higher than at present. The model performed very well at matching the historic data. The results strongly suggest that the transport and transformation of selenium are represented well by the model given its ability to represent different hydrological and load scenarios. For the 1980's conditions, selenite concentrations were higher; however, the particulate selenium concentrations are similar (0.73 $\mu\text{g/g}$ vs. 0.70 $\mu\text{g/g}$). This indicates that particulate selenium concentrations are not just directly proportional to dissolved concentrations, but are related through processes that may be rate-limited.

6.5. ROLE OF BOUNDARY CONDITIONS ON PARTICULATE SELENIUM

The model testing showed that the selected particulate selenium concentrations at the system boundaries (Sacramento River and Golden Gate Bridge) have a significant effect on the predicted particulate selenium concentrations in the water column and the bioaccumulation of selenium by clams. At the same time there is a lack of particulate selenium concentration

measurements on the Sacramento River where the influence of the selenium concentrations in the Delta are negligible (e.g., at Freeport) and in the near-shore area beyond the Golden Gate Bridge. The data deficiency was dealt with by selecting data available from the nearest suitable stations and, using these measurements, selecting the values of particulate selenium for the boundary conditions that provided the best fit to measured concentrations in the Bay.

The best available data to represent particulate selenium concentrations at the riverine boundary are shown in Table 6-1. The salinity of these samples (near zero) from Rio Vista provides an indication that the influence of the conditions further downstream in the Delta is minimized. The lowest value in this data set is 0.357 $\mu\text{g/g}$.

Although the data to characterize the boundary values are limited, data in the bay provide another constraint for the model calibration effort. For the riverine boundary condition at Rio Vista, exploratory runs were performed where particulate selenium varied over a wide range (about 0.2 $\mu\text{g/g}$ to 1.4 $\mu\text{g/g}$ in PSP, Table 4-3). If concentrations at Rio Vista were set at the lowest values in Table 4-3, the water column particulate concentrations could not be matched by the model. The range of plausible values for the Rio Vista boundary is therefore more narrowly constrained by the water column values in the bay.

Table 6-1
Rio Vista Particulate Selenium Concentrations (Source: Doblin et al., 2006)

No.	Date	Salinity	Particulate Selenium ($\mu\text{g/g}$)
1	11/5/97	0.56	0.55
2	6/16/98	0.011	0.357
3	10/7/98	0.017	0.555
4	11/4/99	0.00	0.747

To reflect the uncertainty in the boundary conditions, all simulations were performed with a range of riverine boundary values, albeit not as wide as the one used for exploratory testing in Figure 4-16; the range varied between 0.46 and 0.75 $\mu\text{g/g}$ at Rio Vista.

The particulate selenium concentrations used in the analyses presented in this report are higher than what would be measured in a relatively uncontaminated system, however, this is the range that was consistent with in-bay concentrations. It is clear that there is a need for the best possible characterization of the boundary conditions, especially of particulate selenium, a parameter not always measured in routine monitoring in and around the Delta. The accurate characterization of the particulate concentrations at the boundaries of the system through field sampling efforts is essential to verify the results of this model simulations presented in this report.

6.6. MODEL PREDICTIONS FOR LOAD REDUCTION SCENARIOS

Several illustrative load reduction scenarios were presented to illustrate the relationship between sources and endpoint concentrations (dissolved, particulate, and bivalve concentrations). These load reductions are not proposed TMDL allocations but were meant to provide further insight into the estuary behavior as embodied in this model.

All scenarios consider that the Sacramento River dissolved concentrations are at a regional background level, and that dissolved loads from this source are not modified. Further, boundary values of particulate concentrations for Sacramento River are represented as a range reflecting the uncertainty in this input. For suspended particulates the range in concentrations was 0.46 to 0.75 $\mu\text{g/g}$, and for bed exchangeable particulates, the range was 0.25 to 0.5 $\mu\text{g/g}$. Phytoplankton selenium concentrations were expressed as a Se:C ratio, and set at 15.9 $\mu\text{g/g}$ at the riverine boundary.

With the Sacramento River dissolved concentrations setting the floor, changes were made to dissolved selenium loads from refineries, POTWs and other point sources, local tributaries, and the San Joaquin River. Concentrations were changed separately for the particulate load originating from the Sacramento and San Joaquin Rivers. Although the dissolved and particulate loads were treated separately for the purpose of the load scenarios, once in the estuary, the forms are interrelated through the equations for uptake, mineralization, and adsorption/desorption. However, these transformations are rate limited, with literature or calibrated values of rate constants as detailed in Sections 3 and 4, and given the residence times in the estuary, the uptake rates provide a limit to how fast forms of selenium can change from dissolved to particulate and vice versa. Therefore, the rate-limited formulation results in somewhat different behavior for dissolved and particulate concentrations in the scenarios tested.

When dissolved loads, including point sources and local tributary contributions, are reduced, there are corresponding decreases in the dissolved concentrations, but minimal change in particulate species concentrations. The exception is for a tripling of the San Joaquin River dissolved load: this has a major impact on dissolved phase concentrations, and a smaller, although still significant, impact on the particulate concentrations. In comparison, a decrease of the San Joaquin River dissolved load shows limited impact on dissolved and particulate concentrations, in large part because the decrease is swamped by the contribution of the Sacramento River load. A modification of the scenario with the tripling of the San Joaquin River dissolved load (imposed by changing the concentration, but holding the flow the same as the base case) was performed by allowing delivery of Vernalis-level flows directly to the delta, with no attenuation due to aqueduct withdrawals. This resulted in a similar increase in dissolved and particulate selenium concentrations in the bay.

A tripling and a halving of the Sacramento River particulate load only (the dissolved load was unchanged), showed a major effect on the particulate and bivalve concentrations (an increase and a decrease respectively), and highlights the critical role played by this input, and the need for it to be characterized accurately. This load is different from the other loads in that it is not likely to be modified through specific actions; however, given its importance, it is poorly characterized over the period of the simulation.

Complete reductions in the refinery, POTW, and local tributary loads (Scenario 2), result in decreases in dissolved concentrations under the different flow conditions evaluated. However, the associated particulate concentration changes and clam concentration changes are small. Of the three hydrologic periods considered, the difference was slightly larger for the dry flow month in a dry year, but in all cases the difference as a result of this load reduction was smaller than the simulated variation in the base case.

The overall sensitivity of the estuary to load changes from local tributaries and point sources is greater during dry months, especially during a dry year, i.e., for a given load change factor, greater change is observed during the dry periods. This relates to the lower contribution from the Sacramento River during these periods and the longer residence times in the bay. This highlights the need for focusing on dry periods during which the impacts to the bay may be more easily observed.

Overall, these scenarios provide insight into the representation of the bay in the ECoS model framework, and allow evaluation of the underlying model formulation presented here. They demonstrate the somewhat different behavior of dissolved and particulate selenium over time scales and residence times that pertain to the simulation period, even though it is known that the two phases are inter-related through uptake, mineralization, and adsorption/desorption. In this regard, the model formulation is distinct from the Presser and Luoma (2006) formulation that relates dissolved phase concentrations to particulate concentrations through equilibrium-type partitioning, with dissolved concentrations changes causing immediate and proportional changes in particulate concentrations.

6.7. COMPARISON WITH A SIMPLER MODEL

The model computations of dissolved and particulate selenium could be compared with a somewhat simpler published approach based on linear partitioning between dissolved and particulate phases (Presser and Luoma, 2006). The comparison of this simple approach and the more complex ECoS-based approach highlights the strengths and weaknesses of each. The Presser and Luoma (2006) model is easy to explain to stakeholders and is relatively transparent, which are clearly valuable assets in a TMDL-setting process. However, the model does not fully capture the processes associated with particulate selenium uptake, which influence the results obtained for load changes from the base case. In the linear partitioning approach a reduction in dissolved concentrations results in a proportional reduction in particulate concentrations, a result that is different from the ECoS dynamic uptake/mineralization approach. Data from the mid-80s to the late 90's are supportive of the latter, with decreases in dissolved concentrations not causing observable decreases in particulate concentrations. This feature is also of importance to the TMDL.

6.8. UNCERTAINTIES AND DATA NEEDS

A modeling study, such as the one reported here, provides an opportunity to synthesize information from the system, and in doing so, highlights unknowns that may have a bearing on model predictions. Despite the large amount of data on selenium and its biological uptake in NSFB, there remain significant unknowns that need to be addressed through continued monitoring, as part of future phases of the selenium TMDL. These unknowns are discussed below, and need to be considered during the development of the Implementation Plan for the TMDL. The importance of selenium in the NSFB and the complexity of its behavior are strongly indicative of the need for an active research program in the bay to track these issues.

- **Selenium speciation data:** It is recommended that selenium speciation data for dissolved and particulate selenium along the salinity gradient of the estuary to be collected, at least for a high and low flow year. Particulate selenium speciation at the head of the estuary (e.g., Sacramento River at Rio Vista and San Joaquin River) are

important parameters that need to be sampled under different flow conditions. Such sampling should be conducted each year, with a periodic review of in-bay processes affecting selenium concentrations. Of the particulate forms of selenium, the size ranges that can be ingested by bivalves are of most interest (2-100 μm), and should be considered during the monitoring.

- **Selenium loads:** Selenium loads for different species from the Delta and tributaries remain a large uncertainty, and the vast majority of currently reported measurements are not speciated, and reported as total or dissolved selenium. Dissolved and particulate selenium data with detailed speciation after refinery clean-up are only available for 1999. After 1999, all the available selenium data are in total and dissolved selenium concentrations. Using equations derived for different species of selenium for the Sacramento River at Freeport and San Joaquin River at Vernalis gave good predictions in dissolved selenium concentrations in the Bay. However due to the complexity of the Delta system and the potential transformations occurring in the Delta, selenium loads from the Delta remain uncertain. Riverine inputs of selenium have a large influence on the dissolved and particulate selenium concentrations in the Bay as shown in the sensitivity analysis (Table 4-1). Loads from local tributaries are more significant during high flow than low flow. Uncertainties remain in selenium concentrations and speciation in the tributaries.
- **Selenium transformations:** Transformations of selenium from dissolved to particulate phase through adsorption and phytoplankton uptake are studied less well in marine water than freshwater. There are also uncertainties associated with phytoplankton species with location and time. Seasonal variations in phytoplankton species and selenium uptake by various species of marine phytoplankton are uncertain, as most of the studies were done in freshwater or in the Delta. Cellular selenium concentrations have been reported for some marine phytoplankton species but not all species common in the NSFB.
- **Role of phytoplankton and bacteria in selenium uptake:** Due to limited knowledge on benthic bivalve and zooplankton abundance, the temporal and spatial variability of benthic and zooplankton grazing rates is not well known. The phytoplankton growth formulation, driven by light limitation, uses a single equation across the bay which may not fully represent temporal and spatial variability. It is also recommended that uptake of dissolved selenium by dominant species of phytoplankton and bacteria be studied under the ambient selenium concentrations of the NSFB.
- **Bioaccumulation into the higher trophic levels (fish and birds):** Uncertainties are associated with feeding patterns of the predators due to the migratory nature of certain species (such as surf scoter). Data with good correspondence of time and space in bivalves and predators are sparse. Where dietary concentrations and tissue concentrations can be measured simultaneously, derivation of TTFs can be an appropriate strategy from a modeling standpoint.
- **Sediment deposition and erosion processes:** Sediment deposition and erosion in the NSFB are complicated processes with many unknowns. Deposition and erosion rates can vary significantly over space and time. Erosion can be driven by flow, wind

and tides. Sediment properties (cohesive and non-cohesive) can also affect erosion and deposition. The constructed model currently applied a uniform sediment deposition rate throughout the Bay. The model evaluation results for TSM were considered reasonable for the current selenium TMDL application.

7. POTENTIAL USE OF THE MODEL IN THE SELENIUM TMDL

The calculations described in the preceding pages are the synthesis of a great deal of data and modeling, which was conducted by other researchers over more than two decades. Despite the enormous amount of research attention devoted to selenium in NSFB over this time—as compared to other contaminants for which TMDLs in the region have been developed, such as PCBs and mercury—there still remain some gaps in understanding. At a simple level, one can see these gaps in the calibration and model evaluation figures presented in Section 3, where the behavior of many constituents has not been captured fully, especially when looked at a day-to-day level.

The question for regulators and for developers of the NSFB selenium TMDL is this: Is the model, as presented here, an appropriate tool to further consider in developing load allocations, and monitoring and implementation strategies? Or, are there better ways of representing the system for this TMDL?

It is clearly possible that future development with a more spatially detailed framework and with more detailed characterization of ancillary constituents, such as suspended materials and phytoplankton, may provide a better capability to represent concentrations than has been done in Section 3. Many of these modeling efforts for suspended materials, hydrodynamics, and chlorophyll a, have been ongoing for many years. Although it is feasible to revisit the selenium issue in the future with these calibrated models in hand, it may not occur in the time frame of the selenium TMDL. However, there are data limitations that constrain the potential of future models to fundamentally alter the representation of selenium in NSFB. In particular, adequate calibration of a more detailed selenium model would also require more detailed species level data to be collected in NSFB. Such data have not been collected for nearly a decade, and support for any detailed modeling effort must be contingent on a parallel data collection effort. In the absence of new detailed data, modeling alone may be unlikely to greatly advance the understanding presented here.

The other modeling approach, from a TMDL perspective, is to simplify the system, and treat all sources as entering the head of a well-mixed box, as done by Presser and Luoma (2006). This method has its strengths, not least of which is the ability to communicate the information widely, and to provide a tool where scenario calculations can be rapidly performed on a spreadsheet. This is especially helpful in a regulatory setting where calculations and scenarios need to be evaluated by multiple stakeholders. However, this approach makes other simplifying assumptions, such as treating all selenium species the same way, and estimating particulate selenium with a range of equilibrium partitioning coefficients, that may not reflect our current understanding of behavior in the system. In particular, simulations that we have performed in this report show that influent load reductions, while making changes in the dissolved concentrations in NSFB, have minimal effects on particulate selenium concentrations that are key to the bioaccumulation processes. This finding is driven by the importance of Sacramento River particulate loads in this model, which set a floor for the concentrations observed in the bay. Large load reductions in all non-Sacramento River loads have a limited impact, because the Sacramento River particulate concentrations are still dominant component. However, significant load increases can result in higher particulate concentrations ($\mu\text{g/g}$) in the bay, and are a possibility that

must be considered in TMDL given proposed flow changes in the Delta. Thus, higher flows and therefore loads from the San Joaquin River can reach the bay with the likelihood of higher particulate concentrations, and adverse impacts to the foodweb that depends on benthic filter feeders. Another finding from the modeling, not entirely represented in terms of total particulate selenium, is that efforts to reduce phytoplankton-associated selenium may be more effective at achieving lower concentrations in bivalves because of the relatively high efficiency with which they are assimilated into bivalve tissue.

Given this background, it would appear that there is a role for use of the currently developed ECoS-based NSFBI selenium model in subsequent analyses to be performed by the Regional Board. The analyses that the ECoS-based model could be used for include: development of various load allocation scenarios, for specific numeric targets in fish and development of monitoring strategies to better fill data gaps, such as the limited knowledge of selenium behavior in the Delta. The model can also be used to explore system responses when conditions are very different from current conditions, with higher phytoplankton concentrations, or more extreme dry periods, for example.

To the extent feasible, analyses using this model should be supplemented by other approaches, such as that of Presser and Luoma (2006), and/or other modeling studies that relate to ancillary constituents of relevance to selenium, such as phytoplankton and suspended sediments, as well as other more focused toxicological studies that consider the biological uptake of selenium from bivalves to prey organisms and the internal transport to specific target organs of greatest concern, such as the liver or ovaries (Linville, 2006). Further, these analyses need to be supplemented by more empirical data evaluation approaches, including a “trial and error” approach over an extended period of time, where changes in selenium levels in various biotic and abiotic compartments are closely observed while there are changes in external loading to NSFBI from point and non-point sources. The empirical analysis may provide additional insight into possible approaches for attaining selenium targets in NSFBI biota.

Irrespective of the use of the model in the TMDL, the study has provided an opportunity to gather and analyze a large amount of data from the system and the watersheds that drain into it. This data analysis has identified gaps, discussed previously, that should be addressed in future phases of the TMDL. However, the following general findings are strongly supported by the analysis presented here, including information in the source analysis for selenium (Tetra Tech, 2008a) and the conceptual model of selenium (Tetra Tech, 2008b) that form the basis of the modeling.

- The major riverine inflows to NSFBI (Sacramento and San Joaquin) form the main loads of dissolved selenium. However, dissolved concentrations in the Sacramento River are a tenth of those in San Joaquin River ($\sim 0.07 \mu\text{l}$ compared to $\sim 0.7 \mu\text{l}$). Sacramento River flows are typically several times larger, and the dissolved load contributions from both sources to the Delta are of similar magnitude.
- Particulate selenium concentrations in the riverine flows were directly measured for a limited number of dates. In the Delta, near the Rio Vista boundary of the model and just downstream, the particulate concentrations are $\sim 0.4\text{-}0.5 \mu\text{g}$. These numbers

are elevated further in the estuary with increasing organic fraction in the particulate phase.

- The pathway of most concern from the standpoint of selenium bioaccumulation is the transfer of selenium from particulates to bivalves and the predator species that consume these bivalves.
- The selenium source of most concern in the bay is particulate selenium, which is largely supplied by the riverine loads. Selenium in the water column in the dissolved form may be converted to particulate forms, through phytoplankton uptake and adsorption, but the transformations are highly species specific: selenate interacts minimally with particles, whereas both selenite and organic selenide are more reactive. Should future efforts be focused on the derivation of a partitioning coefficient, or K_d , for selenium, the emphasis must be on deriving species-specific values. If a net K_d is estimated, representing all species of selenium, the value is highly variable depending on the season and flow conditions driven by changing selenium species in the bay.
- The bioaccumulation analysis presents a focused and possibly incomplete evaluation of the adverse effects of selenium uptake on fish and bird species that are benthic feeders. The bivalves chosen for examination in this work, *Corbula amurensis*, are very efficient at bioaccumulating selenium, more so than other bivalve species. In the bioaccumulation analysis, it is assumed that the predator species, white sturgeon and diving ducks, feed exclusively on this bivalve species. Additionally, the prediction of tissue concentrations in white sturgeon and diving ducks does not take into account the observed seasonal differences in bivalve selenium concentrations. The current assessment of risk to predator species in the bay from selenium uptake is largely a result of the presence of *Corbula amurensis*, despite the two-decade long efforts to control non-point sources in the Central Valley and point sources in the bay.
- From the standpoint of managing the selenium impacts to the identified biota in the bay, the most effective option is to control the particulate concentrations, which may not be related in a linear manner to dissolved concentrations. Data from mid 1980s and late 1990s show that large reductions in point source loads decreased dissolved phase concentrations, but had a minimal impact on particulate concentrations.
- The modeling also shows that while decreases in particulate concentration (in $\mu\text{g/g}$) may be difficult to achieve, increases in concentration are possible, should there be increased loads from the San Joaquin basin by means of higher flows into the Delta. Given the range of modifications that are being proposed for the Delta waterways to improve water supplies for export, the likelihood of increased concentrations should be actively considered in the TMDL process.

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APPENDIX 1: CIMIS STATIONS

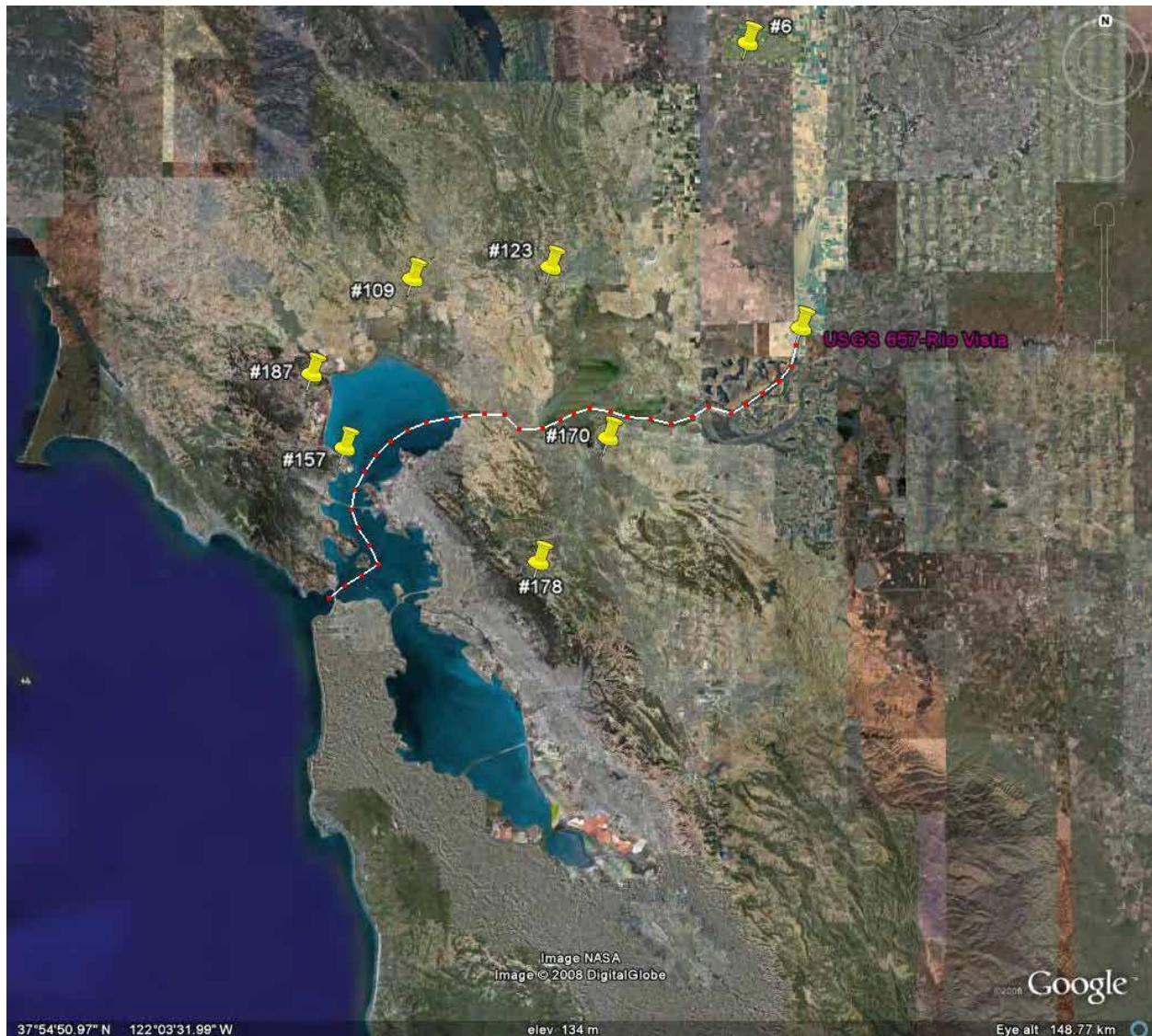


Figure A.1-1 Locations of California Irrigation Management Information System (CIMIS) meteorological stations in the NSFB.

APPENDIX 2: EQUATIONS USED TO SIMULATE ZOOPLANKTON GRAZING

The zooplankton grazing rate is simulated by the model using zooplankton biomass and a modified Ivlev function that predicts the ingestion of phytoplankton per animal (Cloern et al., 1985). The following equation from Meseck (2002) was used:

$$F = 9.5 \times 10^{-4} * W^{0.8} * e^{0.069*(T-10)} * (1 - e^{-0.01*C}) \quad (\text{A.2-1})$$

where T is the temperature (°C), W is the zooplankton weight ($\mu\text{g C/animal}$), and C is the biomass of phytoplankton (mg C/m^3). The weight of the zooplankton varies from 7 to 63 $\mu\text{g C/animal}$.

The total daily zooplankton ingestion, I (mg C/m^3) is calculated using:

$$I = F * Z \quad (\text{A.2-2})$$

where Z is the average zooplankton abundance ($\#/m^3$).

The specific loss of phytoplankton per day by zooplankton grazing (G) is simulated from Cloern et al. (1985)

$$G = -\ln(B-I)/B \quad (\text{A.2-3})$$

with B being the phytoplankton biomass in units of carbon.

Using the equation above resulted in zooplankton grazing rate as high as 0.45/day under chlorophyll a concentration of 2 $\mu\text{g/L}$, temperature of 15 °C, and zooplankton weight of 13 $\mu\text{g C/animal}$. The estimated zooplankton grazing rate is high compared to literature values of 0.01-0.1/day in the bay (Cloern et al., 1985).

APPENDIX 3: EVALUATION OF LEAST SQUARES METHOD

The fitting program used in the model calibration modifies parameter values iteratively, attempting to minimize the sum of square deviations (SSD) from the observed values. To evaluate the effect of starting values in resulting calibrated parameters, SSD values obtained from the calibration process for several parameters are shown in Figure A.3-1 to Figure A.3-5. SSD as a function of different initial values (starting values) for several parameters including dispersion coefficient, scaling factor in simulating velocity of BEPS, San Joaquin River loading constants for organic selenide and selenate, and particulate organic selenide and particulate selenite and selenate are shown. The results indicate that even with different initial parameter values, a similar minimum SSD and calibrated parameter value were reached. This suggested that only one single set of parameters is derived through model calibration and is used in model predictions. The derived value with the lowest SSD was taken as the final calibrated value. The range of SSD was determined by the parameter calibrated (e.g. larger for salinity, in psu and lower for TSP, in g/L).

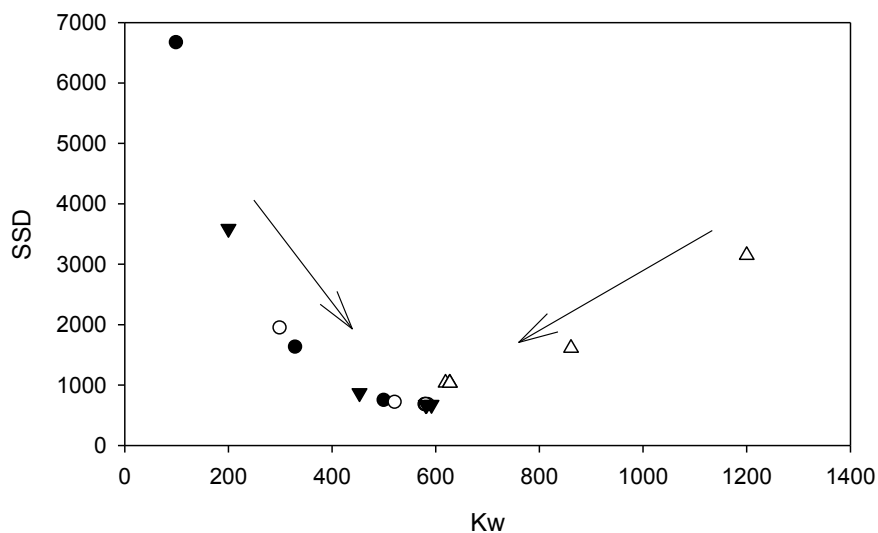


Figure A.3-1 Sum of square deviation as a function starting values in dispersion coefficient. Different symbols represent calibration with different starting values.

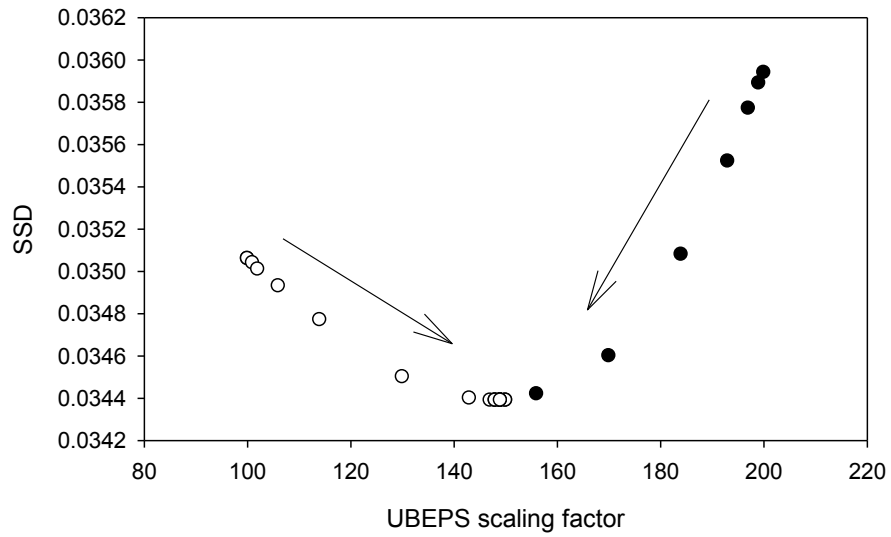


Figure A.3-2 Sum of square deviation as a function of starting values in scaling factor in BEPS. Different symbols represent calibration with different starting values.

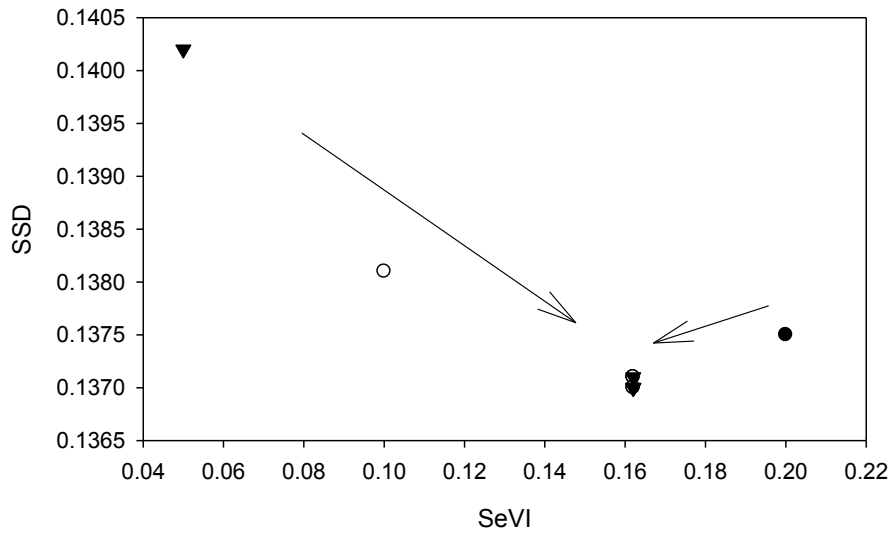


Figure A.3-3 Sum of square deviation as a function of initial values in delta loading constant in selenate. Different symbols represent calibration with different starting values.

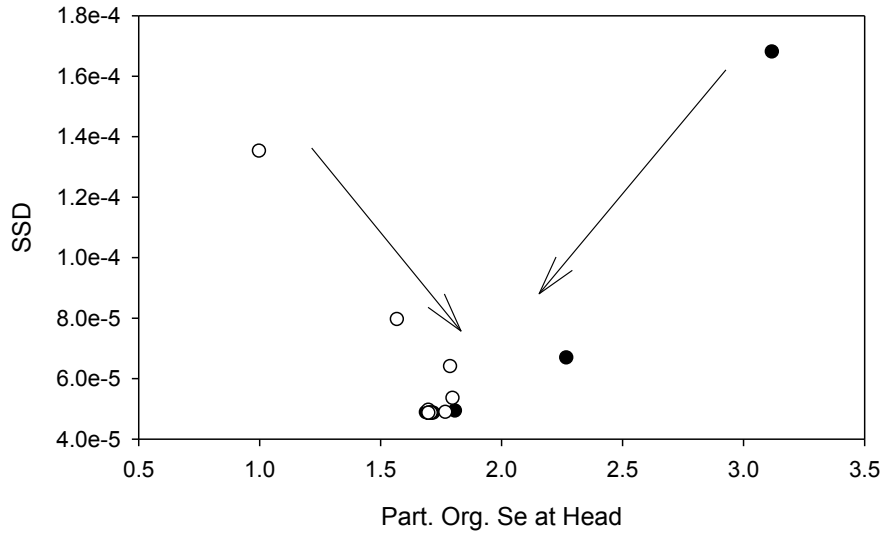


Figure A.3-4 Sum of square deviation as a function of initial values in particulate organic selenide concentrations at head of estuary. Different symbols represent calibration with different starting values.

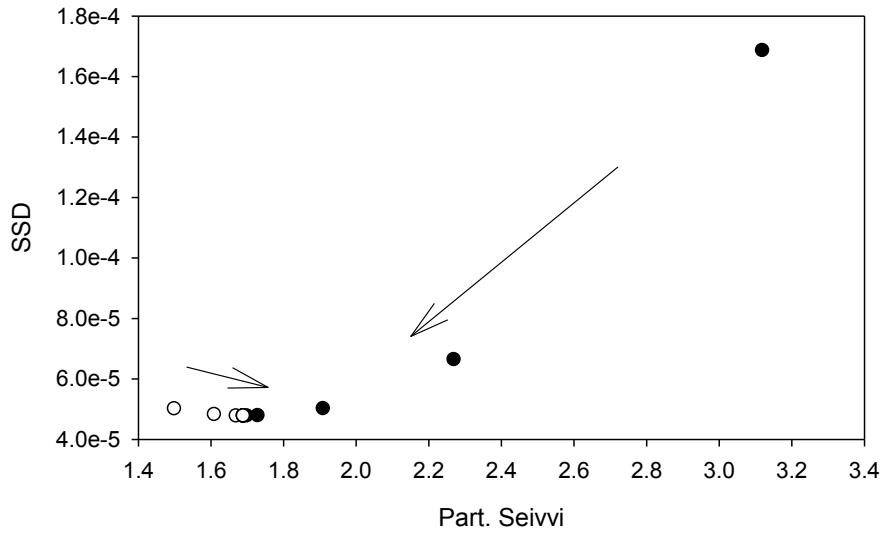


Figure A.3-5 Sum of square deviation as a function of initial values in particulate selenite and selenate concentrations at head. Different symbols indicate different initial values.

APPENDIX 4: RELATIONSHIP BETWEEN DISSOLVED AND PARTICULATE SELENIUM IN THE DELTA

To evaluate potential linkages between dissolved and particulate selenium from the Delta as modeling inputs, dissolved and particulate selenium concentration data by species and ancillary parameters (TSM, chlorophyll a, salinity) collected from sites in the Delta by Doblin et al. (2006) were examined. The data were collected during low and high flow periods of November 1997 to November 1999. As in Doblin et al. (2006), Delta sites were defined as sites upstream of Chipps Island (38° 02.820N, 121° 53.570W).

The relationships between particulate selenium ($\mu\text{g/g}$) and different species of dissolved selenium and ancillary parameters were explored. Total particulate selenium concentrations ($\mu\text{g/g}$) were found to be positively related with selenite, selenate, total dissolved selenium, organic selenide and negatively related with TSM (Figure A.4-1, Table A.4-1). No relationship with chlorophyll a was found if one site with high chlorophyll a concentration was excluded (Figure A.4-2).

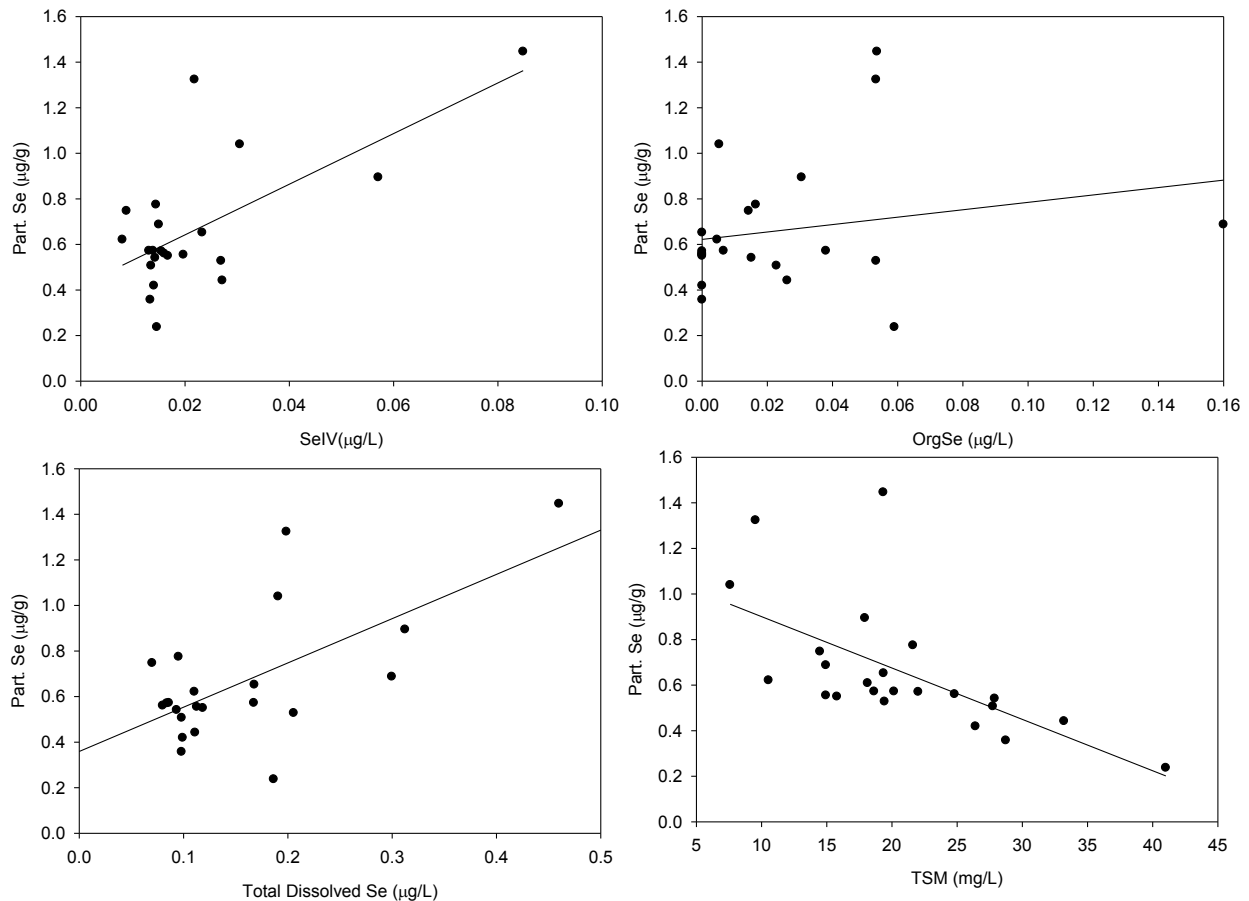


Figure A.4-1 Relationship between particulate selenium and dissolved selenium by species, total dissolved selenium and TSM.

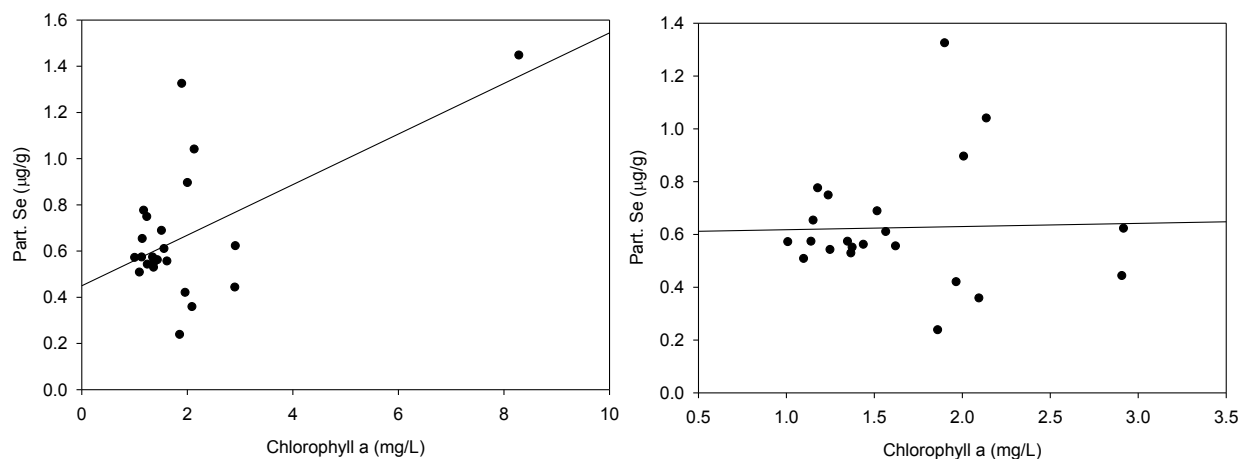


Figure A.4-2 Relationship between particulate selenium concentration and chlorophyll a.

Table A.4-1

Correlation Between Particulate Sselenium and Dissolved Selenium and Ancillary Parameters

Correlation coefficient	Salinity	Se IV	Se VI	Se -II+0	Total Dissolved Se	TSM	Chl a
Total Part. Se (µg/g)	0.05	0.67	0.65	0.20	0.64	-0.62	0.57
PSeivvi (µg/L)	0.02	0.25	-0.18	0.01	-0.10	0.26	0.25
PSe0 (µg/L)	0.12	0.26	0.65	0.13	0.39	-0.24	-0.49
POrgSe (µg/L)	0.18	-0.23	-0.25	-0.07	-0.18	-0.12	0.03

Particulate selenium species in the Delta sites are highly variable, although total particulate selenium shows less variation (Table A.4-2). Particulate organic selenide is highly variable (with CV of 1.006) and is not related to dissolved selenium species or chlorophyll a (Table A.4-2). Particulate elemental selenium shows less variation (CV = 0.674; Table A.4-2) and is positively related to selenate and negatively related to chlorophyll a (Table A.4-2). Particulate adsorbed selenite and selenate show moderate variation (CV = 0.793) and is weakly related to selenite and selenate (Table A.4-2).

Table A.4-2

Particulate Selenium Concentrations by Species and Total Particulate Selenium Concentrations in the Delta (Source: Doblin et al. 2006)

Species	Total Part. Se (µg/L)	Pseivvi (µg/L)	PSe0 (µg/L)	POrgSe (µg/L)
Mean	0.012	0.004	0.006	0.003
Standard Deviation	0.004	0.003	0.004	0.003
CV	0.349	0.793	0.674	1.006
% of Total		31.4	43.6	25.1

The K_d values were species-specific, derived using data collected by Doblin et al (2006) in the Delta. The K_d for particulate adsorbed selenite and selenate ($K_d_PSeivvi$) was based on ratio between particulate adsorbed selenite and selenate concentration ($PSeivvi$) and dissolved selenite (SeIV). The K_d for particulate organic selenide (K_d_POrgSe) was based on

ratio of particulate organic selenide (POrgSe) and selenide (Se-II). K_d values for particulate elemental selenium was derived from concentrations of particulate elemental selenium and selenate. The derived K_d s show different degrees of variability. The average K_d values for each species were used in the model (Table A.4-3).

Table A.4-3
Kd values (L/g) used in linking particulate and dissolved selenium in the riverine inputs.

	Average	Low Flow	High Flow
Kd_PSeivvi	15.73	15.89	15.47
Kd_PorgSe	14.23	16.24	9.30
Kd_Pse0	2.65	3.09	2.16

APPENDIX 5: SUMMARY OF THE TECHNICAL REVIEW COMMITTEE PROCESS

TRC REVIEW OF TECHNICAL MEMORANDUM 6: APPLICATION OF ECoS3 FOR SIMULATION OF SELENIUM FATE AND TRANSPORT IN NORTH SAN FRANCISCO BAY

The establishment of a Technical Review Committee (TRC) was identified in the Project Plan for the North San Francisco Bay Selenium TMDL (RWQCB, 2007) to ensure that the scientific basis of the project and, therefore, key decisions and assumptions, are technically sound. The establishment of the TRC also had the goal of providing an efficient process in which highly specialized expert consultation occurs at key steps in the development of the TMDL. The role of the Technical Review Committee was to provide expert reviews of the modeling process as well as credible technical advice on specific technical issues arising from the review process.

Technical Memorandum 6: Application of ECoS3 for Simulation of Selenium Fate and Transport in North San Francisco Bay (TM6) was the third of the TMDL documents to be reviewed by the Technical Review Committee. Previously, the TRC provided comments on *Technical Memorandum 4. Conceptual Model of Selenium in North San Francisco Bay* and *Technical Memorandum 5. Recommendations for Numerical Model Development*.

The purpose of this appendix is to provide a record of the technical review process, present the comments of the Technical Review Committee members, and to identify the actions that were taken in response to the Technical Review Committee's comments on TM6. This summary documents the rigor of a review process that spanned several months. We believe that by capturing the products of this review process an invaluable source of information will be provided for future investigators.

The members of the TRC were:

- Dr. Nicholas S. Fisher, State University of New York, Stony Brook
- Dr. Regina G. Linville, California State Office of Environmental Health Hazard Assessment
- Dr. Samuel N. Luoma, Emeritus, U.S. Geological Survey
- Dr. John J. Oram, San Francisco Estuary Institute

Resumes for the TRC members are presented in Technical Memorandum 8: Recommendations for the Technical Review Committee (Tetra Tech, 2008). The process of selecting the TRC members is also described in the Technical Memorandum 8.

TM6 TRC REVIEW CHRONOLOGY

The following table identifies the steps in the review process and a guide to the sections describing the process:

1. Draft TM6 Sent to TRC for Review, March 11, 2009	A.5-3
2. TRC Review Meeting Held on April 8, 2009	A.5-3
3. Response to Comments and Revised TM6 Distributed, June 19, 2009.....	A.5-7
3.1. Review of Technical Memorandum 6 by Nicholas Fisher, March 2009	A.5-8
3.2. Preliminary Review of Model Framework (TM-6) by Reggie Linville, April 6, 2009	A.5-13
3.3. Review of Technical Memorandum 6 by Samuel N. Luoma, Emeritus, U. S. Geological Survey, April 13, 2009	A.5-16
3.4. Review of Technical Memorandum 6, John Oram, San Francisco Estuary Institute, Oakland, Ca, April 3, 2009	A.5-20
4. Additional Comments Received from TRC and Responses Prepared, July-August 2009.....	A.5-22
4.1. Comments on the June 19 2009 draft of Technical Memorandum 6, Nicholas Fisher, July 6, 2009.....	A.5-23
4.2. Comments on the June 2009 draft of Technical Memorandum 6 by Regina Linville, August 12, 2009	A.5-26
4.3. Comments on the June 19 2009 draft of Technical Memorandum 6, Samuel N. Luoma, July 6, 2009.....	A.5-36
5. Conference Call with TRC to Discuss Comments and Responses, October 26, 2009.....	A.5-43

5A.1. DRAFT TM6 SENT TO TRC FOR REVIEW, MARCH 11, 2009

The Draft TM6 document, directions for the review process, and a request for written comments were sent to the TRC members in advance of a meeting to discuss their findings. The following questions were provided for the reviewer's consideration during the review process:

1. Are the biogeochemical processes associated with selenium captured adequately in the model formulation? Is there an opportunity for simplifying the formulation further, or is there a need to incorporate additional processes?
2. Is the biological uptake adequately described? Are there better ways of defining the uptake into predator species of interest?
3. Has the model been calibrated and evaluated appropriately? Have all available datasets been utilized? Do you think the level of fits achieved, including poor fits in some instances, are nonetheless adequate for the use of this model in the selenium TMDL?
4. Do the scenarios tested provide enough insight into the model performance? Do you feel a need to consider additional loading scenarios in the modeling report that would enhance understanding of the model performance?
5. Are the strengths and weaknesses of the modeling approach and results clearly laid out?
6. Are there any concerns with the use of this modeling framework in the development of the selenium TMDL in North San Francisco Bay?

A5.2. TRC REVIEW MEETING HELD ON APRIL 8, 2009

A one-day meeting was held with the goal to evaluate the "formulation, calibration, and performance of the modeling tools developed to assess transformation in the North Bay ecosystem in response to changing selenium loads". The meeting consisted of presentations by Tetra Tech, a discussion of the key comments received from TRC members, and a preliminary report to the Regional Water Quality Control Board, San Francisco Bay Region (Water Board) on the findings of the TRC. In addition to the TRC members the attendees included representatives of the TMDL Advisory Committee. The following is a complete list of attendees:

Technical Review Committee Members

Regina Linville, CA State Office of Environmental Health Hazard Assessment
Nicholas Fisher, State University of New York, Stony Brook
John Oram, San Francisco Estuary Institute
Sam Luoma, US Geological Survey

Advisory Committee Representatives

Michael C. S. Eacock (Chris), Bureau of Reclamation, South-Central California Office
Eugenia McNaughton, EPA
Diane Fleck, EPA
Bill Beckon, US Fish and Wildlife Service
Al Middleton, Valero Refinery
Dennis Bolt, Western States Petroleum Association
Timothy Stevens, Department of Fish and Game
Theresa Presser, US Geological Survey
Rosalind Becker, Baykeeper

Regional Water Quality Control Board

Barbara Baginska, Selenium TMDL Project Manager
Naomi Feger, TMDL-Planning Section Lead

Tetra Tech

Tom Grieb, Project Manager
Sujoy Roy, Lead Author - Technical Memorandum 6
Limin Chen, Co-Author and Modeler - Technical Memorandum 6

At the conclusion of the meeting there were three main messages from the TRC. First, the TRC agreed that the model is a legitimate tool to use in building the TMDL, second there is a need to test and to demonstrate the robustness of the model, i.e., to describe how the model is working and to identify the inherent constraints. Third, there needs to be more transparency on how the model works, and the report needs to do a better job of communicating the model results to the stakeholder community.

The results of the TRC review and meeting discussion items are presented below in two parts: (1) a summary of the meeting discussions, and (2) the complete set of TRC comments received and the responses to these comments.

Summary of April 8, 2009 Meeting Discussions

Written and verbal comments from the TRC can be grouped into six primary categories. The following is a summary of specific comments in these six categories and the proposed follow up actions:

Unclear Description of Key Steps in the Modeling Process and of Modeling Assumptions

Here are some of the items/issues identified:

- *How are dissolved Se loads at Vernalis converted to Se concentrations in Bay? (see Section 3.3, p. A.5-16, S. Luoma, Comment 1)*
- *What is the fate of organic Se (biotic) entering the modeled system from the SJR and how is that source incorporated into the model?*
- *An explanation for the “tripling the load” of particulate material scenario is essential. (see Section 3.3, p. A.5-18, S. Luoma, Comment 4)*
- *The slide title “Selenium Loads to Meet Hypothetical Target of 7ug/g Target” (also referred to as the “Green Bar Graph” needs to be better explained. (see Section 3.3, p. A.5-19, S. Luoma, Comment 9)*

Tetra Tech Response: We will focus on explaining better the Delta boundary condition, and the linkage between loads at Vernalis and Freeport, to loads entering the Bay, including particular selenium species that originate in the San Joaquin watershed (e.g., organic and particulate selenide). Similarly, we will add more explanation of the linkage between the dissolved and particulate riverine concentrations at the Delta boundary.

There will be added discussion of the basis of the scenarios, and the scenarios evaluated will be modified to a wider range of particulate loads at the Delta boundary.

An explanation will be added to TM-6 to clarify whether input parameters used represented concentrations or loads and to explain how loads were computed at certain modeling steps.

The section evaluating the impact of various load reductions of a bivalve target of 7 ug/g in the report (Section 5.2), will be revised to explain the approach where loads categories were removed one by one, and to explain the conditions that defined the exceedance of the 7 ug/g target. Graphical presentation of the results will be also revised.

Robustness of the Final Conclusions. The effects of initial conditions and embedded modeling decisions are not clearly described, and it was not clear to the TRC that the effects of the initial conditions were adequately tested.

- “It is very important for the regulatory analyses that different scenarios explicitly *consider* different particulate Se concentrations at the head of the estuary” (S. Luoma, Comment 2)
- “The concentrations of particulate organo-Se should be viewed as

potentially quite variable. That variability should be considered in scenarios concerning influences of changing loads and perhaps in the base calculations. (S. Luoma, Comment 3)

- “But the assumptions, explanation and interpretation of the model results are insufficient for even experts to fully understand”. (S. Luoma, Comment 7)
- The need to better understand the effects of seasonality and wet/dry-year conditions on the modeling results was identified in meeting discussions.

Tetra Tech Response: We will consider a wider range of particulate concentrations at the riverine boundary of the estuary, and will present these results in TM-6.

The role of organo-Se will be discussed through example calculations demonstrating the effect of higher or lower values at a key location (ranging, for example from one-third to three times the model estimated value).

We understand the TRC’s perspective on the need for more transparency. We will add more explanation and/or graphical interpretation at key places in the report, especially on topics relating to the boundary conditions and scenarios, which were the source of many questions at the TRC meeting.

The scenario sections will be modified to include presentations of loading and response values at both annual and seasonal scales.

The uncertainties associated with the model results are not adequately described.

- Express predictions in terms of uncertainties (see Section 3.3, p. A.5-18, S. Luoma, Comment 7). Sam also noted that the report did a good job of listing know/unknowns. We should try to build on this existing description to facilitate a broader understanding of uncertainties.
- In the concluding remarks by the TRC, requests were made to identify uncertainties as well as research and monitoring needs. Identifying these needs from the modeling perspective would make a distinct contribution.

Tetra Tech Response: The revision to TM-6 will carefully consider the role of uncertainty on the major recommendations of the report, and whether these might be influenced by the uncertainty in current understanding of the processes. The development of research and monitoring needs will be a focus of the TMDL development.

The overall conceptual model, captured by ECoS3, is not adequately described.

- One of the consensus items, identified above, was the need to describe how the model is working and to identify the inherent constraints. The TRC suggested that we present a simple box diagram that represents the steps or elements in the model and that provides an explanation of the key equations and the consequences of their inclusion.

Tetra Tech Response: As recommended by the TRC, to aid understanding of model conceptualization, Tetra Tech will include a section representing the

calculations embedded in ECoS at a key location (e.g., near Rio Vista or in Carquinez Strait) with numeric values of the different pools and fluxes, so that the interested reader can better understand the model processes.

The rationale for the selection of model scenarios is not adequately described/defended.

- The report should explain why these scenarios were selected and what the results show in terms of the required regulatory decision-making process.

Tetra Tech Response: The scenarios presented were intended not as specific endpoints for use in the TMDL, but to demonstrate the response of the model to specific inputs. However, given the discussion at the TRC meeting, we propose to present a wider range of boundary conditions and scenarios to meet this objective, and as discussed above, more explanation on what these mean in the real world. The revised model will be used to test specific load-alternation scenarios that the Regional Board may consider in its planning for the TMDL and these results will be presented in a follow-up technical memorandum.

The communication of risks associated with the ecological endpoints is not adequately addressed.

- There were several comments on the characterization of risk and characterization of assumptions, e.g., food sources, as worst case.
- TM-6 needs to explain how the ECoS3 modeling results are used in the assessment of risk to fish and bird receptors. TM-6 could also expand the discussion of ECoS3 modeling results on the ability to meet alternative TMDL numeric endpoints.

Tetra Tech Response: We will review the discussion of risk and risk assessment terminology and address these concerns. The model runs will be updated with inclusion of predictions of concentrations in higher trophic levels that are the preferred target for the selenium TMDL.

A5.3. RESPONSE TO COMMENTS AND REVISED TM6 DISTRIBUTED, JUNE 19, 2009

The written comments received in response to the March 11, 2009 review request (see Item 1 above) were addressed by Tetra Tech and forwarded to the TRC members along with the Revised Draft TM6. The following is the record of comments submitted by the TRC and responses to those comments:

A5.3.1 Review of Technical Memorandum 6 by Nicholas Fisher, March 2009

Tetra Tech responses have been inserted following the reviewer's comments with this exact font and color.

Reviewer's Comment 1: Overall, this document (Technical Memorandum 6) reads like a modeling exercise put together by a team of modelers and environmental engineers rather than by biological and chemical oceanographers. The authors have done a generally fine job in mining the available literature and trying to make sense of it, and I found the document fairly well-written and interesting. As I elaborate below, there are some key details that seem to be skirted over and yet these details may play important roles in the outcome of the model predictions. Most of the details regard information about phytoplankton and Se levels in suspended particles, including species compositional shifts in phytoplankton communities – this may be key, since there are enormous differences among algal species in their ability to take up Se from ambient water – and problems in using Se levels in total particulate matter rather than the phytoplankton, which is what many of the herbivores eat. I believe that the authors recognize that the bioconcentration of Se in particulate matter is key to understanding the subsequent Se loadings in the food web—not the only key, but very important—and in particular it is essential to understand the bioaccumulation of Se in living phytoplankton. This is because it is the phytoplankton, with much variation among species, that concentrate Se appreciably out of the ambient water and convert it rapidly to organic selenides. The organic selenides are the form of Se that is assimilated very appreciably by the herbivores, and it is noteworthy that many herbivores are often quite selective in their feeding on phytoplankton (as opposed to all suspended particles). I also propose a possible straightforward solution – a solution which would need to be tested in the field – to addressing this uncertainty without investing heavily in examining the species compositional changes over space and time in phytoplankton communities.

Tetra Tech Response: We are in full agreement with the reviewer's comment regarding the role of phytoplankton in controlling selenium bioaccumulation. In response, we have made numerous changes in TM-6, including descriptions of selenium uptake as determined in published laboratory studies, an analysis of selenium uptake by consideration of different phytoplankton species, and consideration of a wide range of uptake rates (up to a hundred times greater than the rate used for the base case). Analysis using selenium:carbon ratios that have been determined for different species, shows that the values that are consistent with observations in the bay are in the high range of laboratory measurements (15-30 $\mu\text{g/g Se:C}$). Values that are much lower than this range result in calculated particulate selenium concentrations that are significantly lower than observed values (Section 4.7).

Reviewer's Comment 2: Below I list comments on the document in the order in which these issues appear in the document. I have put an asterisk next to those issues that I consider to be most significant.

Page 1-8 (4th bullet), as I noted previously, it is inappropriate to use K_d values for Se, at least for Se taken up by phytoplankton. This is because Se uptake is an energy-requiring process—the Se is not in equilibrium between particle surfaces and the dissolved phase (there is no appreciable passive uptake of Se by

phytoplankton: Fisher & Wente 1993), and because once Se is taken up by cells it is rapidly converted to organic selenides (mostly selenoamino acids), and so the organic selenides inside the cells are clearly not the same species of Se as the inorganic selenite that was taken up by the cells and they are therefore not in equilibrium. I noted that problems with using Kd values was noted by the authors later in the document.

Tetra Tech Response: The uptake of Se is modeled using first order rate constants. The Kd values were used for comparison with other studies.

Reviewer's Comment 3: Page 2-8, top paragraph: "Data on microbial uptake of Se was not available in the bay." This is not correct—see Baines et al. (2004).

Tetra Tech Response: The uptake rates measured in Baines et al. (2004) were for the Delta water only. Phytoplankton and microbial communities in the Delta may be very different from that in the Bay (due to marine water influence).

Reviewer's Comment 4: Page 2-9, Table 2-1: Why are Riedel selenite uptake rates 10 times higher than those of Baines et al. (2004). Is this attributable to the fact that Riedel used algal cultures, whereas Baines used natural phytoplankton assemblages, consisting almost surely of some non-living material?

Tetra Tech Response: The rates reported in the original papers are absolute rates, not rate constants normalized to ambient selenite concentration. The difference in rates is due to several reasons:

- a. Different sources of phytoplankton species used in the culture
- b. Different ambient selenite concentrations used in the culture (10 ug/L vs. 0.3 ug/L).
- c. Different chlorophyll concentrations used in the experiment.

When normalized to ambient selenite concentration, the rates of uptake are higher from Baines et al. (2004).

In the revised TM-6, rates are reported in consistent units, normalized to chlorophyll a and selenite concentrations.

Reviewer's Comment 5: Page 2-12, Table 2-2: incomplete, many species not shown.

Tetra Tech Response: The species shown are for the 0.15nM experiment (Table 3 and 5 in Baines and Fisher, 2001).

Reviewer's Comment 6: Page 2-13: I do not understand Eq. 31—how was that arrived at?

Tetra Tech Response: The equation assumes sine wave concentration of selenium concentrations. The concentration varies from a mean concentration with certain period/frequency. It is the equation originally used in Meseck (2002) and does not imply mechanistic significance; it is primarily a fitting function.

Reviewer's Comment 7: *Page 3-2, Table 3-2: Why use Riedel et al's selenite and organic selenide uptake rates by phytoplankton instead of Baines'? Note that Riedel's study was with freshwater phytoplankton.

Tetra Tech Response: From a calibration standpoint, the reason for using Riedel's rates is that they gave results consistent with observations in the bay. The

uptake rate is an important link between dissolved and particulate concentrations. In the revision to TM-6, we consider a range of values of uptake rate (reaching values up to 100 times higher than Riedel's rates) to evaluate the impact on overall calibration. This analysis (Section 4.3) found that increases in uptake rate must be matched by increases in calibrated mineralization rate, failing which both dissolved concentrations and Se:C ratios are significantly different from observed values. This analysis provides support for a general range of uptake rates that are applicable for the bay, and indicates that the uptake rate to mineralization rate ratio needs to be approximately constant for other variables to remain consistent with observed values.

Reviewer's Comment 8: **Page 3-7: Riedel uptake rates were higher, not lower (see Table 3-2) than Baines' rates. Also, Riedel used freshwater algae—how applicable is this for North San Francisco Bay? Also, it is important to keep in mind that Se:C ratios in the field are for seston, much of which is NOT phytoplankton. Dead organic aggregates will have high C concentrations but will not be effective in taking Se up out of ambient water. Se:C ratios in living algae should be much greater than that in seston, and it's often the phytoplankton that are ingested by herbivores (not total seston), so it is important to know the phytoplankton Se concentrations (not just seston). I realize this is a tricky business, but it is possible to determine this with current technology (for example, using x-ray fluorescence microscopy with a synchrotron), although this is very specialized, somewhat expensive, and time-consuming (see Twining et al. 2003). It does provide definitive and unambiguous answers, however. As well it is dependent upon getting sufficient "beam time" on the appropriate synchrotron (such as at the Advanced Photon Source at Argonne National Laboratory); nevertheless, it is do-able. Currently though it is clear that the available data base on phytoplankton Se loads is lacking, and models to understand and predict impacts of Se biogeochemistry in San Francisco Bay will be necessarily limited as a consequence.*

Tetra Tech Response: Based on the responses above, when normalized for selenite and chlorophyll a concentrations, the Baines et al. (2004) rates are higher than the Riedel et al (1996) rates (Table 2-1 in TM-6). The key test for the use of these rates in this work is whether they can be used to explain the particulate and the dissolved concentrations. If the uptake rates are too high, the particulate concentrations, and the Se:C ratios will be exceeded, and the dissolved concentrations will be too low. Likewise, if the uptake rates are too low, the dissolved concentrations will be exceeded and the particulate concentrations will be too low. Another control on the particulate and dissolved concentrations is the mineralization rate of selenium that has been taken up by plankton, i.e., the rate at which particulate organic selenide is converted to dissolved selenite. For the simulated values to remain consistent with observations, the best fit uptake/mineralization rates ratios are similar. The main point of this exercise is that the calibration can be used to bound the range of uptake rates and mineralization rates, and that these are in the range of values reported from controlled laboratory studies.

Additional analysis with the model also provides ranges of plankton Se:C ratios that are consistent with particulate selenium data (all species). A test of these ratios with direct synchrotron measurements of Se:C ratios in live algal cells from the bay would be an intriguing comparison.

Reviewer's Comment 9: So, a thought: organic selenides in particulates are key (that is what is assimilated so efficiently from phytoplankton into herbivores) and

they probably represent mostly phytoplankton Se. The other forms of Se (inorganic and elemental) are probably sorbed to non-living material and won't be an important Se source for animals. By knowing the particulate organic selenide load, it is possible to evaluate most of the Se that is likely to be bioavailable for the animals in phytoplankton, regardless of their taxonomy. Using this approach for the purpose of modeling, we may not need to know the phytoplankton species composition and track its changes spatially and temporally (tedious work, and very time-consuming). The particulate organic selenide load will almost certainly be associated primarily with intact phytoplankton (potential food for the herbivores). Not only is there a problem in looking at seston vs. phytoplankton for understanding Se but there is also a problem with the non-specificity of using chlorophyll a as a measure of phytoplanktonic Se. That is because all taxonomic groups of algae have chlorophyll a—thus this pigment is a pretty good indicator of total algal biomass. However, we know from Baines and Fisher's (2001) paper (cited in this document) that there are very large differences (up to 4-5 orders of magnitude) among different phytoplankton types. Chlorophytes (green algae), in particular, display much lower Se concentrations than most diatoms, dinoflagellates, coccolithophores, and other algal groups. Thus, relating Se accumulation with chlorophyll a can be very misleading, depending on the algal species that happen to be dominating a particular body of water at a particular time. Bear in mind that phytoplankton species composition (not just biomass) in many bodies of water changes substantially with season, and so the bioavailable organic selenides could also change seasonally, depending on the composition of the algal communities being considered. Therefore, a key missing piece of information in this document (at least, I didn't see it) is the species composition of the algal community in different regions and seasons. This may well be known (Lehman's work, perhaps? Cloern's?) and should be factored in to the models if species composition data are available. Or, as noted above, you could consider relying on the organic selenide load associated with total suspended particulate matter.

Tetra Tech Response: The current data in the bay can be used to infer temporal distributions of phytoplankton species or groups, such as diatoms, chlorophytes, cyanophytes, and flagellate algae (Lehman, 2000). The dominant species of phytoplankton vary across space and time. The general finding is that diatoms, green, bluegreen and chrysophyte are more abundant during wet and normal years. While during dry years, cryptophytes, green flagellates, and miscellaneous flagellates are more abundant. Selenium concentrations in phytoplankton generally follow the order of: golden brown algae > dinoflagellates > diatoms > green algae. The increase of golden brown algae and green algae in recent years may have different effects on particulate selenium concentrations associated with phytoplankton. However selenium concentrations in flagellates have not been measured. When data from 1999 are evaluated, the particulate selenium data provide a strong basis for allowable value of Se:C ratios, typically 15 μ g/g or greater. Values at the low end of the Se:C ratio spectrum result in particulate selenium lower than observed. The modeling exercise provides a means to evaluate the laboratory results, and suggest further experimentation, especially when Se:C ratios have been determined for specific concentrations only, and are known to vary with concentration.

The suggestion for measuring particulate organic selenide directly as a surrogate for species of direct relevance to clam uptake is a good one. However, we are

strongly in favor of more selenium species data in the bay in general, and would even support the measurement of particulate selenium (all species) as a starting point (addressed in Section 6.7).

We are aware of the difference in Se:C ratios in seston and phytoplankton. The model simulates Se:C ratios in phytoplankton only and were compared to measured Se:C in phytoplankton for a few species that are present in the Bay (Cryptomonas sp. – golden brown algae; Prorocentrum minimum- dinoflagellates).

Reviewer's Comment 10: Page 3-38: I'm curious—why did the riverine Se loadings drop 2-5 fold after 1998?

Tetra Tech Response: This is largely due to change in flows.

Reviewer's Comment 11: Page 3-56: Poor fits for particulate organic selenides—attributable to different algal species (see above)?

Tetra Tech Response: We are unable to explain the poor fits, not the large variation in organic selenides in the bay at stations in close proximity to one another. This may be a result of local-scale processes that are not captured in the model, including local-scale algal species variation, or may be a result of the analytical technique used to determine particulate organic selenide (by difference from adsorbed selenate+selenite and elemental selenium).

Reviewer's Comment 12: *Page 4-8: Need for characterization of phytoplankton types—should do simulations for different types of phytoplankton, not just varying chlorophyll a.

Tetra Tech Response: We have performed this in Section 4.7.

Reviewer's Comment 13: Page 5-7: Stewart & Luoma (2008) not in reference section.

Tetra Tech Response: There is an error in the reference. Should be Stewart and Luoma not M.Jagger.

Reviewer's Comment 14: Page 5-11 to 5-14: I found it hard to follow the argument being presented on these pages.

Tetra Tech Response: This section has been revised extensively.

Reviewer's Comment 15: Page 5-14 to 5-15: As noted earlier, can't use Kds; meaningless to use Kds for organic selenides where particulate Se form is organic and ambient dissolved Se is inorganic.

Tetra Tech Response: This section has been deleted.

Reviewer's Comment 16: *An important question: What is the fate of the phytoplankton entering the Bay-Delta system from rivers, especially once they hit saline waters? Presumably these cells are enriched in organic selenides, where the Se was originally obtained from the rivers, but once they reach saline waters, do they rapidly die and is the Se associated with them remineralized? I assume that *Corbula amurensis* is eating estuarine/marine phytoplankton species, not the freshwater cells that may have washed into the system from the rivers.

Tetra Tech Response: In the model, phytoplankton are treated as a single constituent through chlorophyll a. When riverine phytoplankton enter the bay, the selenium initially remains in the organic particulate compartment, and is mineralized over time. Selenium is also added to the algal compartment through

uptake. Phytoplankton growth and decay, in aggregate, is tracked in the model, as is phytoplankton-associated selenium. However, for the purpose of the calculation, the algae are treated as a single species.

Reviewer's Comment 17: *Another question: if the levels of Se loading that need to be reduced are deemed unrealistic, does this mean that Se levels in San Francisco Bay were always dangerous to diving ducks and sturgeon and other fish that ate benthic bivalves, or has the story hinged primarily on the introduction of *Corbula amurensis*, which tends to bioconcentrate Se to higher levels than other bivalve species? If the latter, then more research on the biology of *C. amurensis* may be as useful as investing heavily in reducing Se loadings via the rivers, with the hope that some strategies may develop to reduce their populations and thus reduce the conduit of organic selenides to wildlife and fish. This is not meant to support the idea that we should do nothing about Se loadings—in fact we should do everything possible to reduce them—but a parallel effort, if it is feasible and will do less harm than good, to reduce the populations of this invader species may also be money well spent.

Tetra Tech Response: Based on available information, the high bioaccumulation in *Corbula amurensis* is an important cause of high levels in predator species. The control of invasive species along with possible load modifications is an alternative that the Regional Board may choose to address during the implementation phase of the TMDL. Note that the other common clam species present in the bay and Delta, more on the freshwater side, *Corbicula fluminea*, is also an invasive species throughout much of the United States.

References cited not already in document:

Fisher, N.S., and M. Wente. 1993. The release of trace elements by dying marine phytoplankton. *Deep-Sea Research* 40: 671-694.

Twining, B.S., S.B. Baines, N.S. Fisher, J. Maser, S. Vogt, C. Jacobsen, A. Tovar-Sanchez, and S.A. Sañudo-Wilhelmy. 2003. Quantifying trace elements in individual aquatic protist cells with a synchrotron x-ray fluorescence microprobe. *Analytical Chemistry* 75: 3806-3816.

A5.3.2 Review of Technical Memorandum 6 by Regina Linville, April 6, 2009

Tetra Tech responses have been inserted following the reviewer's comments with this highlighting.

Reviewer's Comment 1: *The following is provided as a preliminary review of the major issues. The discussions during our upcoming meeting should clarify several issues and raise additional questions. This report reflects the large amount of work performed by the authors and previous modelers on the loading, fate and transport, and bioavailability of selenium in northern San Francisco Bay. The authors have provided a good description of the major factors involved in these processes. Similarly, a thorough analysis of the modeling framework is provided.*

I have outlined my concerns below and look forward to discussing these with the authors and review committee.

A5.3.2.1 The critical role of phytoplankton

The report contains a good description of the importance of phytoplankton in the overall bioavailability of selenium. It appears that the model does not provide a mechanism to distinguish the relative importance of “particulate organic selenide” as phytoplankton compared to suspended sediment (importance to bivalve accumulation). Is that true?

Tetra Tech Response: Phytoplankton associated particulate organic selenide has the same assimilation efficiency with other forms of particulate organic selenide. The assimilation efficiency of these forms of selenium is different from that associated with inorganic forms (adsorbed selenate and selenite and elemental selenium). The role of particulate selenium speciation in clam uptake is clarified further in Section 2.7.

Reviewer’s Comment 2: *Section 4.3 addresses part of this question, but it would be helpful to extend that analysis to the influence on predicted bivalve and predator bioaccumulation. Similarly, the loading that most impacts the phytoplankton fraction of particulate organic selenide if of high interest.*

Tetra Tech Response: Modeled values in bivalves and predator species are shown in Section 3.4. The scenario analysis in Section 5.1 includes now includes analysis of impacts to bivalves for all cases considered.

Reviewer’s Comment 3: *I would like to further discuss the treatment of phytoplankton and particulate material in the model.*

Tetra Tech Response: The analysis of phytoplankton species as well as uptake rates has been expanded in Sections 4.3 and 4.7.

A5.3.2.2 Model framework and risk assessment

Reviewer’s Comment 4: *The bird toxicity reference values (TRVs) and hazard quotients (HQs) in birds are referred to as highly conservative. I disagree. How are these TRVs conservative? In the study used for the TRV (Heinz et al., 1989) the LOAEL (~ 0.7 mg/Kg-day) resulted in malformations in 7% of unhatched eggs compared with < 1% in controls (NOAEL is ~ 0.3 mg/Kg-day). The next dose level (~ 1.4 mg/Kg-day) resulted in malformations in 68% of unhatched eggs. These values are very close together, which is consistent of our knowledge of selenium toxicity in general (i.e., narrow range between nutritional and toxic values). Additionally, the assumption that 100% of diving duck’s diet consists of clams is not particularly conservative. The authors statement that “. . . there are a large number of conservative assumptions that are incorporated in the estimated HQs. Therefore, HQs that are in the single digits (i.e., <10) are often not considered to represent significant risks.” is not supported (nor is it a general assumption in ecological risk assessment). For example, a HQ of 2 based on the NOAEL TRV corresponds to a dose that is equal to the observed LOAEL (and 7% of eggs with malformations). A HQ of 2 based on the LOAEL TRV corresponds to a dose that resulted in malformations in 68% of unhatched eggs.*

Tetra Tech Response: The language has been modified to: “An HQ less than 1 indicates that there is a negligible potential for adverse ecological impacts due to exposure to a particular COPEC, whereas an HQ greater than 1 indicates that there is a potential for adverse ecological impacts due to exposure to that COPEC.

However, there are a large number of conservative assumptions that are incorporated in the estimated HQs and a value slightly greater than 1 does not indicate significant risk. ”

Reviewer’s Comment 5: *The development of the TRV was not described in this document or in TM-3. (However, these TRVs are very similar than those developed by EPA Region 9’s Biological Technical Assistance Group (BTAG), which are used by DTSC. See:*

http://www.dtsc.ca.gov/AssessingRisk/upload/Eco_Btag-mammal-bird-TRV-table.pdf.

I suggest either providing a detailed justification of the TRV development, or using the BTAG numbers.

Tetra Tech Response: The text has been modified to clearly define the TRVs used in the work. This exposure study used in this calculation is the same as that used by BTAG (Heinz et al., 1989).

Reviewer’s Comment 6: *More information is needed regarding the Trophic Transfer Factors.*

Tetra Tech Response: General guidance on the TTFs used in this work was provided by Sam Luoma and Theresa Presser, based on a review they are developing. A more complete citation will be presented when available.

Reviewer’s Comment 7: *The authors refer to the exposure scenario as a **worst case scenario** since it is based on the accumulation by, and consumption of, *Corbula amurensis*. This seems to suggest that the predicted exposure would only happen under extreme (‘the worst’) circumstances. *Corbula* is the main species of bivalve in the study area and a dominant prey item of diving ducks and sturgeon. A more clear description would be that the modeled scenario applies specifically to top predators of the benthic food web.*

Tetra Tech Response: The terminology worst case scenario is no longer used in the report. Language similar to that suggested here is used in Section 7 to summarize the results of this aspect of the analysis. The following language is used: “The bioaccumulation analysis presents a focused and possibly incomplete evaluation of the adverse effects of selenium uptake on fish and bird species that are benthic feeders. The bivalves chosen for examination in this work, *Corbula amurensis*, are very efficient at bioaccumulating selenium, more so than other bivalve species. In the bioaccumulation analysis, it is assumed that the predator species, white sturgeon and diving ducks, feed exclusively on this bivalve species. Additionally, the prediction of tissue concentrations in white sturgeon and diving ducks does not take into account the observed seasonal differences in bivalve selenium concentrations. The current assessment of risk to predator species in the bay from selenium uptake is largely a result of the presence of *Corbula amurensis*, despite the two-decade long efforts to control non-point sources in the Central Valley and point sources in the bay.”.

Reviewer’s Comment 8: *I would like to discuss these issues further and their implications in the model framework.*

A5.3.2.3 Model calibration and evaluation

Reviewer's Comment 9: *I have several questions regarding the calibration and evaluation section that I suspect will be clarified during our meeting. The questions involve the choice of parameters, specific calculations, and calibration details.*

A major concern in this section is the lack of comparisons between observed and predicted values in top predators. My concern regarding the discussion of risk is described above.

Tetra Tech Response: Model predicted selenium concentration in predators are compared with available data in Section 3.4.

A5.3.2.4 Model predictions and proposed uses

Reviewer's Comment 10: *I have several questions regarding model predictions and proposed uses that will likely be answered during Tetra Tech's presentation on Wednesday.*

I would like to discuss some of the general conclusions in light of the sensitivities identified in the report. An example is the prediction that particulate selenium will not respond to a decrease in selenium loading. The authors highlight the implications of this prediction in the executive summary and elsewhere. However, it appears that prediction of selenium in phytoplankton is one of the weaker functions of this model. Is the emphasis justified considering the known limitations of this model?

Tetra Tech Response: The role of phytoplankton uptake in the model is evaluated in much more detail in the revised TM-6, Section 4, providing more support for the general conclusion.

A5.3.3 Review of Technical Memorandum 6 by Samuel N. Luoma, Emeritus, U. S. Geological Survey, April 13, 2009

Tetra Tech responses have been inserted following the reviewer's comments with this exact font and color.

Reviewer's Comment 1: *Model description is unclear about how dissolved Se loads at Vernalis are converted to Se concentrations in Bay. A factor is inserted for Delta removal. Is this tied to some physical process? Is it a constant? What is the value of the removal "constant"?*

Tetra Tech Response: Figure 2-16, Concentrations and flows used to compute loads of selenium, dissolved and particulate, and by species, for the Sacramento and San Joaquin Rivers, has been added to TM-6. This figure includes a summary of the methods used to calculate the dissolved concentrations and loads to the North Bay (confluence) based on 1999 speciation data from Vernalis. For the San Joaquin River, the dissolved concentrations at the confluence were calculated by multiplying the dissolved selenium concentrations at Vernalis by an input constant (1 – removal constant). Separate input constants, presented in Table 3-3, were used for the three species in the dissolved phase: SeIV (0.326), SeVI (0.26), SeII (0.534). The loads at the confluence were calculated by multiplying the "new" dissolved concentrations by the flow (difference between the Net Delta Outflow Index and flow from the Sacramento River at Rio Vista) at the confluence. Dissolved concentrations in the Bay are then determined by the advection, dispersion and transformation equations described in Section 2.

Reviewer's Comment 2: *As we discussed repeatedly, it is very important for the regulatory analyses that different scenarios explicitly consider different particulate Se concentrations at the head of the estuary. As it stands, every analysis of effects of changing Se load in the rivers only considers the effect of that load on the slope in Fig. 3-43. Unless the river boundary condition is explicitly changed, the y-intercept will always stay the same in plots like 3-43. i.e. Several riverine-boundary-condition-particulate-Se-concentrations should be considered with each scenario wherein effects of changing loads in the river are considered. The final conclusions cannot be robust until this factor is better taken into account.*

Tetra Tech Response: Section 4-4, Varying seawater and riverine boundary particulate selenium concentrations, was added to TM-6. The effects of higher and lower bounds of riverine concentrations for different selenium species were investigated. The sensitivity analyses conducted include the evaluation of the effects of different endmember particulate concentrations on simulated particulate selenium concentrations (Figure 4-15) and selenium concentrations in bivalves (Figure 4-16).

Reviewer's Comment 3A: *It is a little worrisome for the TMDL that the model cannot explain the high variability in ug/g Se in particulates, in particular in particulate organo-Se. The concentrations of particulate organo-Se should be viewed as potentially quite variable. That variability should be considered in scenarios concerning influences of changing loads and perhaps in the base calculations. For example, it appears that 0.468 ug/g was chosen as the Se concentration for PSP. This is at the lowest end of the range of concentration that Doblin et al observed at the upstream end of their sampling. What would happen to the final conclusion (reducing loads make little difference) if you started with a PSP-Se of 0.8 or the maximum of 1.5 ug/g. If you start at a higher riverine endmember isn't easier to have an impact if you reduce loads from the river.*

Tetra Tech Response: Lower and higher boundary conditions for riverine and seawater endmember concentrations were simulated. The results of varying the endmember concentrations on model simulated particulate selenium concentrations are presented in Section 4. The effects of changes to the endmember concentrations on the comparisons of base case results with reduction in point-source loads are presented in Section 5.

Reviewer's Comment 3B: *Need to adjust marine endmember. Just as the riverine endmember is probably too low, the marine endmember is probably too high. The open ocean, where these data (Cutter and Bruland, 1984) are from is completely phytoplankton and their detritus (no inorganic component). The coastal zone is likely to have lower Se concentrations. Why not use a mean of the Doblin observed values at the seaward-most site, along with and higher riverine boundary condition to directly test the effect of reducing loads? The important problem here is that one cannot differentiate the effect of internal productivity changes vs the ocean endmember in determining the positive slope for the particulate (ug/g) with salinity.*

Tetra Tech Response: The original calibration of the model resulted in the selection of a seawater boundary value of 1.22 ug/g for particulate selenium. In Section 4.4.1 the model simulations are re-run using a particulate selenium concentrations measured at the Golden Gate by Doblin et al (2006) as the endmember concentration for particulate selenium (~0.9 ug/g). Simulated

selenium particulate selenium concentrations in the water column and selenium concentrations in bivalves show some differences from the original simulations. The results are presented in Figures 4-12 through 4-14.

Reviewer's Comment 4: *It is essential that the scenario of "tripling the load" of particulate material be explained. What was done here. What was tripled. What was the TSM condition? What is the mix of particulate species. Why is the intercept only doubled when the concentration is tripled? I would like to see a table that shows the steady state uptake from each type of particulate Se; perhaps it would be easier then to see. I think we understood this by the end of the day, but other readers will not understand it.*

Tetra Tech Response: Table 5-1 was prepared to more fully describe the loading factors used for each of the scenarios. In Scenario 7, for example, the riverine particulate selenium loads consisting of BEPS, PSP and Phytoplankton were increased by a factor of three.

Reviewer's Comment 5: *What happens when nutrients inputs increase, as they might if SJR inflows rise?*

Tetra Tech Response: We did not change the concentration of nutrients in these scenario model runs. A large effort would be required to adequately address the nutrient question, and the focus of this report is the examination of the ability of this model to address the behavior of selenium in the North Bay. A series of specific questions regarding the interaction of increased nutrient concentrations and selenium loading

scenarios could be addressed in subsequent analyses that are planned as part of the TMDL effort.

Reviewer's Comment 6: *Is the model useful? Decent job; very useful effort with state of science. The problem is not in the model; it is legitimate. But the assumptions, explanation and interpretation of the model results are insufficient for even experts to fully understand. The base cases also need to be rerun with different boundary conditions, as suggested above. How important are those boundary conditions to the final conclusions?*

Tetra Tech Response: Sections 4 and 5 have been revised to address these questions regarding the effects of changing boundary conditions, and the descriptions of the results have been enhanced to provide support for the conclusions presented in Section 6.

Reviewer's Comment 7: *Express predictions in terms of uncertainties. Values range from this to this under condition 1 and condition 2 (reasonable for system). Identify where we need data to reduce uncertainty.*

Tetra Tech Response: The presentation of the results in Section 5 (e.g., Figures 5-3 – 5-5) was revised to show the range of effects from modifying the magnitude of the loads from the various sources. In Section 7, recommendations are made for additional efforts to reduce uncertainties and increase the understanding of the factors that affect selenium biogeochemistry in the Bay.

Reviewer's Comment 8: *Are conclusions robust. We are not convinced that final conclusion is fully tested in a robust fashion. An important limitation is the disconnect between dissolved load changes and particulate concentrations at the riverine boundary condition. If it is implicitly assumed that PSP-Se does not*

change with load changes, that makes it almost inevitable that it is pragmatically impossible to reduce exposures below those seen in 1999. Ways to address that:

- a. Conceptual model with equations or terms listed.
- b. Scenarios must manipulate PSP Se concentrations at the riverine boundary conditions. Capture high flow/low flow.
- c. Test sensitivity to ocean end member; down to low value.
- d. Important uncertainties. Good job of listing known/unknowns, but don't mention time. No data beyond 1999.
- e. We hope that the the TMDL recommends research, monitoring and triennial review of important scientific uncertainties and what have we learned from science. Are knowledge gaps addressable with current technology.

Tetra Tech Response: As noted above, numerous changes have been made to the report to address the effects of changing boundary conditions, to describe the scenarios in more details, and to describe the sources (e.g., Figures 4-31 – 4-33), and to describe the processes related to phytoplankton of dissolved species (e.g., Figure 4-8). Additional graphics and descriptions were added to enhance the conceptual model. For example, these additions have been made to this version of TM-6: representation of selenium exchanges between different compartments in each cell of the model (Figure 2-5), graphic depiction of the model cells and the representation of boundary conditions (Figure 2-9 and Box 3), and enhanced description of the concentration and flows used to compute loads (Figure 2-16).

Reviewer's Comment 9: Green bar graph showing necessary reductions of particulate load shows huge reductions are required to meet targets. It is not transparent how this was done, even to we "experts". It must be explicitly and simply described because this is a major conclusion. In the meeting we heard that $ug/g * gTSM = load$. What happens if one a) starts with 1.5 ug/g at the riverine boundary, b) calibrate to the clam scenario wherein the data best fit (probably a lower IR) then c) reduced the concentration in river boundary condition in model by say half using the calibrated clam IR. Could you reach the target more feasibly? The most important conclusions are based upon this.

Tetra Tech Response: This figure has been replaced with a more detailed description of the effects of changing boundary conditions and additional loading scenarios in Sections 4 and 5.

Reviewer's Comment 10: It is also important to do the above seasonally. The conclusion about little responsiveness to loads must be done for low flows alone.

Tetra Tech Response: In Section 5, the response of the system to changes in loading has been evaluated for seasonal variation and extremes in flow conditions.

Reviewer's Comment 11: Choice of TTF-fish. Perhaps run with both 1.1 and 1.7 TTF for sturgeon in different scenarios.

Tetra Tech Response: In Section 3.4, the model is run to compare predictions with data for white sturgeon muscle tissue, white sturgeon liver tissue, and scarp muscle tissue. There is variability in the model predictions based on variability in the clam concentrations. At this time, the simulations are performed with single

values of TTF (1.7 for white sturgeon muscle tissue and 1.8 for scap tissue), although as the role of the modeling in the TMDL is finalized, additional runs could be performed with a range of TTFs.

Reviewer's Comment 12: *The choices of scenarios by the regulatory/stakeholder community will be critical in outcomes from the model and ultimately in conclusions about allocating sources of Se.*

Tetra Tech Response: The scenarios we have presented are illustrative, and intended to demonstrate model behavior. Specific loading scenarios can be run in a future phase.

Reviewer's Comment 13: *The model has helped us understand the data. Iteration should continue into the future.*

A5.3.4 Review of Technical Memorandum 6, John Oram, San Francisco Estuary Institute, Oakland, CA, April 3, 2009

Tetra Tech responses have been inserted following the reviewer's comments with this exact font and color.

Reviewer's General Comment: *Overall, the report is thorough, well-written, and interesting. The graphics are effective; they portray the information in a simple and clean manner. The authors are commended for drafting such a detailed report. Model development is well-documented and/or referenced. Enough information is given that the approach could be reproduced. Model testing was well-thought-out, executed, and documented. Results are effectively conveyed in writing and graphics. My specific critiques are as follows:*

Reviewer's Comment 1: *The document did not discuss the collective Delta sediment work of Lester McKee and Dave Schoellhamer (I believe it is McKee 2004). They have been observing sediment loads at Mallard Island for years. Their findings are relevant to how Delta sediment loads are handled in this model.*

Tetra Tech Response: The reviewer raised a good point. Particulate selenium loads from the Delta are important. We discussed the McKee et al. work in an earlier memo (TM2). However we agreed with the reviewer that the work is relevant here and should be discussed again in this document. In TM2, we used annual TSS loads from Delta estimated by McKee et al. (2006) and particulate selenium concentrations measured by Doblin et al. (2006) to estimate particulate selenium loads from Delta. The model used a function relating flow and TSS to estimated TSS concentrations and selenium concentrations on particulates to estimate particulate selenium loads. Our preliminary comparison of the data suggested loads estimated using the two methods agree relatively well. This is now shown in Section 2.10.

Reviewer's Comment 2: *Se in fish and diving ducks are the main drivers of the Se TMDL (correct?). Yet presentation of model results and model testing focused mostly on examination of physical parameters (e.g., Salinity, TSM, Se in water) and not on Se in fish and diving ducks. A stronger link between the physical parameters and Se in biota could be presented. It is difficult to judge if this model is appropriate without knowing how relevant certain findings are to the biota endpoints. For example, the model misses the ETM and Central Bay chl-a concentrations on relatively short time-scales. However, it is hard to say how important it is to get these features right without knowing how they effect biota*

concentrations. Bioaccumulation is not necessarily a fast process. If the shorter time-scale processes of the ETM don't affect biota Se concentrations greatly than missing the ETM is not that important. However, if the ETM is important to Se uptake by biota then the model needs to do better.

Tetra Tech Response: Selenium in fish and diving ducks were related to selenium concentrations in bivalves through several methods: linear regression relationships from Presser and Luoma (2006), a trophic transfer factor (TTF) and risk assessment approach.

We have now shown the model predicted selenium concentrations in sturgeon livers and surf scoter livers in Section 3.7. based on a more exhaustive analysis of the food web concentrations, it appears that the model does capture key features of the biological data, and that inadequacies in matching the peaks for TSM do not translate into systematic errors in tissue concentration predictions.

Reviewer's Comment 3: *Chl-a concentrations are predicted relatively well by the model. The biggest shortcomings are in Central Bay during late summer and early fall. There is speculation (by Cloern, Jassby, Oram, and others) that Central Bay phytoplankton blooms during this time of year could be driven by coastal upwelling outside the Golden Gate. Inoculation of Central Bay waters and/or transport of nutrient rich waters into Central Bay could play a large role in these blooms.*

My comment #2 applies here as well. It is hard to judge how important this is. I suspect it is important. We are talking about seasonal blooms that are relatively long-lasting. Certainly long enough for filter feeders to consume the phytoplankton and for zooplankton to graze.

Tetra Tech Response: The goal of the modeling is to represent the chlorophyll a concentrations with a small number of parameters, including growth and grazing rates which were driven by the same underlying forces for each year of the simulation. It is possible to adjust some of these parameters on a year-to-year basis, or to modify their spatial variation to more closely fit the data. This could help explain the selenium concentrations in biota, although there remains a data gap in that we do not have water column selenium data for all years of the simulation. Given the paucity of selenium data, our preference is to use a set calibration for this work, i.e., values are not adjusted locally to fit local peaks. This approach helps explain a considerable amount of the variability in the biological data over time (seasonally and inter-annually). Future work may consider some of these processes in more detail.

Reviewer's Comment 4: *Why was such a short time period used for model calibration (one year)? It is common to use roughly 60% of your observation data for model calibration and 40% for validation. It seems that model performance could be improved if the model were calibrated to a longer (and more diverse) calibration data set.*

Tetra Tech Response: The selenium speciation data are only available up until 1999. No speciation data exist after 1999. Speciation data for previous years 1997-1998 were used in model hindcast and represent different refinery load conditions.

Reviewer's Comment 5: *I have to say that the developers did a fine job of model testing. I am a big proponent of such tests, as they help build confidence in results. And in this case the testing results make intuitive sense, and thus build my*

confidence in the model. But, again, I am missing the link to fish and diving ducks. While the testing convinces me of the physics of the model and prioritizes data gaps for the physical model they do not tell me how important these data gaps are for biotic endpoints.

Tetra Tech Response: The model predicted selenium concentrations in livers of fish and diving ducks have now been added to the revised TM-6.

A5.4 ADDITIONAL COMMENTS RECEIVED FROM TRC AND RESPONSES PREPARED, JULY-AUGUST 2009

Additional comments on the Revised Draft TM6 document were received from three of the TRC members. Responses were prepared to these comments and together this information provided the basis for discussions at a teleconference meeting with the TRC, Tetra Tech and the Water Board (see Item 5 below).

A5.4.1 Comments on the June 19 2009 draft of Technical Memorandum 6, Nicholas Fisher, July 6, 2009

Tetra Tech responses are inserted in this color and font.

Reviewer's Comment 1: *I have read through the modifications of the document and think that most of the points I raised were adequately handled. The revised version which considers a range of selenite uptake rate values is an improvement. The conclusion that is drawn that remineralization rates need to increase in proportion (approx.) to increased uptake rates is interesting. It suggests future research that could be conducted to test this speculation, and that is one of the purposes of models (in my opinion). However, it is not clear to me that remineralization will result in release of selenite from cells. Since all the selenite that is taken up by cells is converted to organic selenides, the release of Se from cells will almost certainly be in the form of organic selenides, not selenite. The rate at which the released organic form gets converted to selenite is questionable, but data from the open ocean at least suggest that this rate may be very low. Looking at Cutter's data, in some open ocean waters the selenite levels can be far lower than the organic selenide levels. And speaking of remineralization, you note that "when riverine phytoplankton enters the bay, the selenium initially remains in the organic particulate compartment, and is mineralized over time." While this certainly strikes me as plausible (provided that the cells are not eaten first!), I am unaware of any published direct measurements that support this contention. Maybe I'm missing something?*

Tetra Tech Response: In the model formulation, the remineralization of particulate organic selenide results in releases of dissolved organic selenide, not selenite. The dissolved organic selenide is converted to selenite through an oxidation rate. The rate used in the model is set at a value of 0.004/day. Therefore, mineralization will result in organic selenide, which is slowly converted to selenite. This is now noted above Eq 23 on page 2-13.

The turnover of selenium by phytoplankton is considered to be quick (Fisher and Reinfelder, 1991). This quick turnover will allow intracellular and extracellular Se(II) pools to reach isotopic equilibrium (Baines et al. 2004). The release of organic selenide from the cells can be taken up again by phytoplankton. When riverine phytoplankton enter the bay, they may be grazed upon or go through processes that mineralize intracellular particulate organic selenide to dissolved organic selenide and uptake of dissolved organic selenide.

In one study (Vandermeulen and Foda, 1988), selenium release back into the medium by algae accounts for as much as 35% of the total selenium found in the external medium. After 10 days incubation, about 30.6% of labeled selenium was found in cells and 67.6% was found in cell-free filtrate for the *Thalassiosira* sp. For *Cachonina* sp., about 65.6% of labeled selenium was found in cells, while 27.5% was found in cell-free filtrates. In the cell free filtrates, 10.4% was found in live cell filtrates as selenite, while total amino acids, free amino acids and chloroform soluble forms account for 9.6%, 4.0% and 2.3% of the labeled selenium. Although the release of selenium metabolites from algae have not been measured in the field, it has been measured in the lab.

Reviewer's Comment 2: *Your point on the relative bioaccumulation of Se by different forms of algae is correct, but I fear slightly misleading. While the general*

order you note (“golden brown algae > dinoflagellates > diatoms > green algae”) may be right, it is also worth noting that the data suggest that there can be big differences within groups—notably for diatoms, witness *Skeletonema costatum* vs. *Thalassiosira pseudonana*). Furthermore, data in Baines & Fisher (2001) suggest that the green algae are able to regulate their Se levels better than the other forms—not only are bioconcentration factors lower for these cells, but the absolute Se levels per cell appear to remain more constant over a 30-fold exposure range (0.15 nM vs. 4.5 nM selenite) (see their Fig. 3).

Tetra Tech Response: The general order is to provide only a rough grouping. We revised the text (p2-14) that different species of diatom can vary significantly, and that the grouping is an approximate guide.

We tested the influence of phytoplankton species on predicted particulate organic selenide concentrations and influence is large (section 4). When the dominant phytoplankton species is golden brown, predicted particulate selenium concentrations are closer to observed values.

Reviewer’s Comment 3: *Partially for this reason, I still think that the determinations of particulate organic selenide would be very telling in terms of assessing the bioavailable Se potential for the bivalves. As interesting as it is to follow the bioconcentration of Se by different forms of phytoplankton (and near and dear to my heart), the ultimate story must be related to the total particulate organic selenide levels, provided that it is in particles that the bivalves normally can ingest (roughly 2-100 µm), depending on the animal. In other words, knowing the organic selenide levels in large seston “pieces” that are mm in scale would probably not be very useful.*

Tetra Tech Response: The temporal and spatial composition of phytoplankton species is not easy to model. Although we can make model runs representing a variety of species, any assumptions about the presence of specific phytoplankton species at any given time and place will be always problematic. If we make some assumptions of the dominant phytoplankton species with respect to time and space, we can do a simulation based on that assumption. Given the complexity in phytoplankton species with respect to time and space, it is difficult to make general assumptions with regard to the phytoplankton species. In long-term data collected in the bay, it has been noted that during wet and normal years, diatoms, greens, blue greens and chrysophytes dominate, while during dry and critically dry years, cryptophytes (golden brown), green flagellates and miscellaneous flagellates dominate (Lehman 1996). Therefore we can test a simplified scenario which assumes golden brown algae dominate during dry years, and green algae dominate during wet years. We can discuss this with the TRC, or include this in the proposed TM-7 which will contain additional model runs.

The point about the size classification of particulate selenium is valuable from the monitoring standpoint and is discussed in Section 6.7 on page 6-4 and 6-5 (Data needs).

Reviewer’s Comment 4: *I have a question about the data presented in Table 2-1 and suggest a few modest changes to that table. It remains somewhat unclear to me why Reidel et al. (1996) measurements are used, since their experiments relied on wholly unrealistic Se concentrations (10 µg/l). The information shown in the 4th row, (uptake of dissolved selenite by phytoplankton), the top row within the box (for Riedel et al and Baines et al) gives uptake rates not adjusted for ambient*

Se concentrations. The bottom row within the same box shows the data normalized to ambient Se levels—however, this was not clear and I struggled for a while to understand how these data were produced from the original papers. Now, I understand them, but the document may benefit for further clarity on how these numbers were generated—perhaps a footnote to the table? Perhaps more importantly, the data for Baines et al. (2004) present data for microbial (mostly bacteria we believe) and phytoplankton uptake data (respectively, 0.2 - 1 μm and > 1 μm fractions). The data shown in TM6 only show the results from one of the two sample sites (“Channel” site) but fail to show the data from the other site (“Chlorophyll maximum”). There is not basis for excluding one of the sites, and I suggest that the table be revised to include them both. Keeping with the format as it stands now, the minimum uptake rate should be 0.15 [NOT 0.33 $\text{pmol Se}/\mu\text{g chl/hr}$]—that is, if both sites are included. However, I think it also valid to only include the phytoplankton data for this table (note that the descriptor in column 3 is “Uptake of dissolved selenite by phytoplankton.” If only the phytoplankton (> 1 μm fraction) are used, then the values range from 0.07 - 0.21 $\text{pmol Se}/\mu\text{g chl/hr}$. My calculations show that this translates to a rate constant of 225.8 - 777.8 l/g chl/hr , taking into consideration the ambient selenite concentration in each location and time (Table 1 of Baines et al., plus the added 0.03 nM of radioactive selenite).

Tetra Tech Response: We revised the table on page 2-10 to include data from both sampling sites.

The reviewer makes a good point that rates from Baines et al. when normalized to ambient selenium concentrations (which are more realistic to San Francisco Bay conditions) can be quite large (225.8 – 777.8 l/g chl/hr). We tested the model with varying selenium uptake and mineralization rates to illustrate the effects of using a different uptake rates on particulate selenium simulation (shown in Section 4.3). The test results suggested that when selenium uptake rates were increased to this rate, mineralization rates needed to be raised by approximately the same factor, in order to produce a reasonable selenium concentration on particulates. Thus, when uptake rates are high, the transformation of POrgSe back to selenate is not fast enough to predict a realistic selenate concentration in the bay. Reported mineralization rates for particulate organic Se (as you noted in comments above) are low at least in open ocean. Although the ambient concentrations used in Riedel et al. experiment are unrealistically high and for freshwater phytoplankton, they seem to produce reasonable selenium concentrations on particulates without using high mineralization rates. The values thus used were based in part on the literature and in part on the calibration.

With respect to values cited from Baines et al. (2004), we included the value for the channel site at first simply because the site has a phytoplankton level closer to the conditions in the bay (2 $\mu\text{g/L}$) rather than 12-30 $\mu\text{g/L}$ observed in the other study site (“chlorophyll maximum”). The rates measured when normalized to chlorophyll a concentrations however are similar between the two sites. When estimating the uptake rates, we include both phytoplankton uptake and bacteria uptake for the reason that some bacteria uptake may also exist in the Bay and could contribute to high particulate selenium concentrations. However, since we are comparing only phytoplankton uptake rates here, we could make the changes to include phytoplankton uptake only. Section 4.3 has been updated to reflect this discussion.

A5.4.2 *Comments on the June 2009 draft of Technical Memorandum 6 by Regina Linville, August 12, 2009*

Tetra Tech responses are inserted in this color and font.

Tetra Tech Response: We thank the reviewer for her thorough assessment of our report and associated comments. A principal concern raised in this review is related to the relative magnitude of particulate selenium that is present as permanently suspended particles (abbreviated as PSP and generated primarily in the riverine sources) versus that present in living phytoplankton. PSP is comprised of inorganic and organic components including planktonic detritus. It is the reviewer's point that much of the particulate organic selenium in the bay is associated with phytoplankton, and that, at the very least, we are overestimating the contribution of organic selenium in PSP in the model development. Our primary response, explained in more detail below, is that the relative magnitude of the phytoplankton selenium and PSP-selenium is based on the best data we have, and is significantly constrained by the calibration of the model, where concentrations for multiple selenium species, both dissolved and particulate, were matched to observations in the bay.

Reviewer's Comment 1: *Particulate organic selenium in permanently suspended particles.* *Particulate organic selenium (Se) in permanently suspended particles (PSP) appears to be overestimated in this model. In conceptual models of the bay, particulate organic Se is mainly considered to be associated with living phytoplankton. In TM6, particulate organic Se enters NSFB from the rivers as both PSP and phytoplankton. Based on discussions with the authors, particulate organic Se associated with PSP is assumed to be Se in detritus. In a separate model calculation, riverine particulate organic Se associated with phytoplankton is estimated based on chlorophyll-a (Chl-a), carbon to Chl-a ratio and Se to carbon ratio.*

Tetra Tech Response: We do not think that particulate organic Se is mainly associated with living phytoplankton. The reviewer didn't provide a reference for the statement "In conceptual models of the bay, particulate organic Se is mainly considered to be associated with living phytoplankton," which would be helpful to our work.

Note that lab tests with bivalves and different forms of particulate selenium have shown assimilation from living and non-living sources (Table 2-4 in TM-6 report and references cited therein).

As measured by Doblin et al. (2006), chlorophyll a (representing living phytoplankton) is at approximately the same concentration of phaeophytin indicating the presence of relatively high level of detritus. Total particulate organic carbon measured in the estuary is only accounted for by 20-30% of carbon associated with living phytoplankton. Therefore in the model, we assumed particulate organic Se to be associated with both living phytoplankton and detritus. And a large portion of the living phytoplankton and detritus in the Bay enters from the Delta.

Particulate organic Se in PSP (defined as permanently suspended particles) was derived as the difference between total particulate organic Se and particulate organic Se associated with phytoplankton. Therefore it is unlikely to be overestimated unless phytoplankton associated particulate organic Se is underestimated.

Reviewer's Comment 2: The example in Table 1 of these comments (see Appendix 6) shows that PSP-associated particulate organic Se (detritus) has a very large impact on overall particulate organic Se concentrations in the model. Using the average flow of November 1999, an estimated PSP concentration of 0.010 g/l and the model parameters for Se associated with PSP (Table 3-3 of TM6), the amount of particulate organic Se contributed by riverine PSP is 56 g/day. Using the same flow rate, a Chl-a concentration of 1.2 µg/L (approximate mid-point of Nov 1999 Delta samples in Doblin et al., 2006) and the Baines et al., 2004 conversion of 15.9 ug Se/g C – the particulate organic Se load from Sacramento River phytoplankton is 33 g/d. In this example, the particulate organic Se contributed by riverine PSP (56 g/d) is greater than that of riverine phytoplankton (33 g/d). [Note, I used an approximate median value for low-flow Chl-a from Doblin. Using the complete range of low-flow Chl-a observed by Doblin, the phytoplankton Se contribution varies from much lower than to greater than that of PSP particulate organic Se]. **And most importantly, the particulate organic Se associated with PSP is defined by the riverine concentration throughout the entire estuary (eq. 23).** The concentration of particulate organic Se associated with PSP is mainly impacted by the rate of mineralization to dissolved organic Se (k_1), which is relatively small (0.0066/day).

Tetra Tech Response: The reviewer used single day values to illustrate that PSP-associated particulate organic Se (detritus) is higher than the phytoplankton associated Se. This is not how the two sources are accounted for in the model. Both PSP and phytoplankton concentrations from riverine sources can vary through time. The date selected by the reviewer reflects a relatively low Chl a concentration of 1.2 ug/L. As shown in Figure 3-8 of TM-6, observed Chl a concentration by Doblin et al. at the head of estuary were at higher concentrations of 4 ug/L for many of the months. As a result, the estimated particulate organic Se associated with phytoplankton could be much higher than 33 g/d for other dates. Tables 1-5 from the reviewer were included in the Appendix (see page 26 in this document).

The reviewer is concerned about the fraction of selenium associated with organic forms. Living phytoplankton carbon accounts for only 20-30% of particulate organic carbon (POC) measured at Rio Vista by Doblin et al. (2006). Therefore, other sources of POC (e.g. detritus of plant material, microbes) make a significant contribution to the fraction of Se associated with organic forms (POrgSe).

Eq. 23 computes a mass loading of particulate organic Se from the river that is added to the Se pool in the estuary (on daily basis), once in the estuary, it is subject to transformations such as mineralization and uptake (in addition to transport advection and dispersion). We labeled the terms in Eq.23 that are associated with riverine inputs. Eq. 23 represents inputs from rivers and in-situ transformations.

We revised section 2.5 (p 2-11) to clarify these points.

Reviewer's Comment 3: Figures 4-20 and 4-21 of TM6 help to clarify my concern here. These figures show the simulated particulate Se in the estuary due to PSP, suspended bed sediments (BEPS) and phytoplankton in both ug/L and ug/g. Tables 2 and 3 of these comments show my estimations of the relative sources of particulate Se **assimilated into clams** based on the simulations shown in Figures 4-20 and 4-21. My method for estimating these values is explained in the

footnote.1 In Figure 4-20, the spatial distribution of particulate Se is simulated using November 1999 estuary conditions (low flow). It appears that particulate organic Se from PSP accounts for roughly 22 – 31% of the total Se assimilated by clams and 37 – 46% of the organic Se assimilated (see Table 2 here). Figure 4-21 provides simulated particulate Se concentrations at Carquinez Strait during high and low flow (see Table 3 here). High flow (June 1998 & March 1999) particulate organic Se from PSP accounts for roughly 39 & 45% of the total Se assimilated by calms and 61 & 82% of the organic Se assimilated. Particulate organic Se in PSP does not change very much in the modeled estuary so the large contribution of particulate organic Se from PSP will minimize the impact of decreased Se concentrations in phytoplankton. By freezing a large proportion of organic Se, I think the model loses the ability to detect small but relevant changes in particulate Se. (Note: the estimates of particulate organic Se associated with PSP at greater salinities will likely be artificially high because selenite is absorbed onto PSP as it passes through the estuary. The main point here is that the organic Se associated with PSP does not **decrease** very much after it enters the estuary.)

Tetra Tech Response: Sediment contribution of selenium originates from two sources: sediments entering the estuary from the rivers and sediments generated from bed exchange processes in the estuary. The riverine inputs of suspended sediments and sediment contribution from bed exchange are treated separately in the model. Also, composition of selenium in these two sources of sediments is likely to be different. Figures 4-20 and 4-21 show the concentrations of total particulate selenium from river PSP, bed exchange sediments and phytoplankton.

Riverine suspended sediments contain particulate organic selenide, adsorbed selenite + selenate, and elemental selenium. Sediments from the bed are dominated by elemental selenium; however they also contain a fraction of particulate organic selenide and adsorbed selenite + selenate. The sediment contribution often referred to in other references is the sediment contribution from bed exchange only.

The load inputs of sediments from the Delta to the Bay have been estimated by other investigators to be large sources, ranging from 0.26 to 2.6 Mt/yr (McKee et al. 2006). USGS water data reports provide estimates of the annual suspended sediment load measured at Freeport. For water year 07-08 the sediment load was ~0.3 Mt/yr while for 05-06 water year it was ~2.9 Mt/yr. These studies suggest that the amount of selenium associated with suspended sediment from the Sacramento River can be large and highly variable. Selenium associated with this large sediment source can be overlooked. We don't think the particulate selenium associated with detritus is out of place. Detritus concentrations measured by Doblin et al. (2006) as shown in Figure 4-41 of TM-6 first decrease but then increase toward the seaward boundary.

Additional clarifications are identified below:

1. The contribution of selenium from bed sediments through bed exchange (erosion) is an independent process from riverine inputs of suspended sediments. When estimating roles of sediments to particulate selenium, these two processes should be separated, as in Doblin et al. (2006).
2. The increase of particulate organic Se through the estuary (or limited decrease) is supported by the observed data (Figure 3-26 of TM-6). Particulate organic selenium measured by Doblin et al. (2006) showed an increasing trend through

the estuary. Whether this increase is due to fast mineralization of particulate organic selenium to dissolved organic selenium and rapid uptake by phytoplankton to form living particulate organic selenium or slow mineralization, the observed particulate organic selenium concentrations (in $\mu\text{g/g}$) increase through the estuary. Moreover, the uptake of selenite and organic selenide is higher than other species of selenium. A fast turnover of particulate organic selenium needs to be balanced by relatively fast selenium uptake rates to maintain the particulate organic selenium concentration. When uptake rates of selenite exceed 10x the rates used in the model, the transformation of selenite is limited by the oxidation of organic selenide to selenite. This, in turn, will result in predicting lower selenite concentrations than observed in the Bay (Figure 4-10 of TM-6).

3. The PSP associated particulate organic selenium is not fixed by the riverine particulate organic selenium concentrations. The relatively slow mineralization rate was derived through balanced calibration and is within the literature range (k_1 , Table 3-3 in TM-6).

Reviewer's Comment 4: Simulated Selenium in Phytoplankton. *In the model, riverine (freshwater) phytoplankton continues to grow and uptake Se throughout NSFB. The likelihood of this actually happening is highly dependent on flow, since most freshwater phytoplankton species have limited salinity tolerances. During lower flows, many riverine phytoplankton species will be affected by increased salinity in NSFB and will not continue to function (i.e., take up Se). Treating riverine phytoplankton as estuarine phytoplankton is likely to overestimate the influence of the Sacramento Rv. during lower flows.*

Tetra Tech Response: The model simulates overall phytoplankton concentrations, as represented by chlorophyll a in the estuary by season relatively well. As discussed in the model evaluation section, variations in phytoplankton concentrations by season show good agreement with the measured data (Figure 3-23 of TM-6). Therefore the overall phytoplankton concentrations during low flow are not over-predicted.

The reviewer suggests that during low flow conditions (higher salinities) freshwater phytoplankton may not be able to function. This is true. Indeed, across any spatial and temporal gradient in the estuary changes in the species of phytoplankton occur and a shift from freshwater to marine species is common. More subtle shifts in response to water chemistry and temperature are also taking place. The model does not represent the inter-species dynamics of algae in the Delta and bay. Both freshwater and marine phytoplankton is represented in the model as "one compartment" and these are tracked through the chlorophyll a levels.

The observed phytoplankton concentrations may be lower during low flow and these concentrations are reproduced well by the model. The selenium associated with riverine phytoplankton inputs is still accountable as riverine contribution, regardless whether it remains as living phytoplankton or detritus after it enters the estuary. The contribution of riverine phytoplankton selenium is estimated as loads of selenium associated with phytoplankton entering from the rivers. The model formulation section related to this topic (Section 2.6) has been edited to reflect this discussion.

Reviewer's Comment 5: *Potential load reductions scenarios will not impact Se loading from Sacramento Rv. phytoplankton. Is there a way to limit the active uptake of Se by riverine phytoplankton to freshwater areas in the model (i.e., link it with flow)?*

Tetra Tech Response: It is possible to limit riverine phytoplankton uptake of selenium to the freshwater area (e.g. at salinity < 1.0) by changing the uptake rates. However we still need to simulate uptake of selenium by marine phytoplankton, as long as there is phytoplankton in the estuary. Passive uptake of selenium by phytoplankton is also possible (Riedel et al. 1996). In the model, phytoplankton are treated as a single component and not treated as two groups of species (marine and freshwater). The reasons behind this simplification are explained in Section 2.6.

Reviewer's Comment 6: *Additionally, the explanation of uptake rates of dissolved Se by phytoplankton ($k_4 - k_6$) is unclear. Uptake rates from Riedel et al. (1996) and Baines et al. (2004) are shown in Table 2-1 using different units. The significance of the different units and justification of the choice of rates needs clarification.*

Tetra Tech Response: The uptake rates are shown in both the units reported in the original papers and using a uniform unit (shown in parenthesis; l/g chl a/hr). We chose to show the rates in original units for easy comparison to the original references and also showed the two rates in common units for comparing rates from these two sources.

We revised the text to reflect this point (p 2-9).

Reviewer's Comment 7: *Considering that the measured uptake of Se in different phytoplankton species varies by an order of 10^5 , and the model is not able to capture changes in phytoplankton composition, is this approach truly an improvement over the simplified approach developed by Presser and Luoma (2006)? I think this is a very important question to consider.*

Tetra Tech Response: The model provides a framework for testing the influence of changing phytoplankton composition, even though the current parameterization is limited by knowledge of phytoplankton species composition and selenium concentration in species in NSFB.

The model also provides mechanisms to simulate spatial and temporal variations in phytoplankton concentrations through the bay, which is not easily achieved by the simple model. In addition, selenium dynamics are not determined by phytoplankton alone. The model provides mechanisms to simulate constituents such as salinity and TSM, and loads and different species of selenium (particulate organic, particulate elemental, particulate adsorbed selenite + selenate, dissolved organic selenide, selenite and selenate).

The model is compared to the Presser and Luoma results (Section 5.3). The discussion in Section 5.3 and in the new Section 6.7 is updated to reflect the pros and cons of using a more complex model.

Reviewer's Comment 8: Boundary Conditions - Riverine Boundary. *I am still unclear regarding the authors choice of the Se to carbon ratio (Se:C) used to simulate organic Se concentrations in riverine phytoplankton. The selected Se:C of 15.9 $\mu\text{g Se/g C}$ from Baines et al. (2004) is much higher than the range of < 1 to 4.4*

$\mu\text{g Se/g C}$ from cultured phytoplankton in Doblin et al. (2006). Doblin exposed the phytoplankton to 90nM Se or $\sim 7\mu\text{g Se/L}$, which is higher than concentrations found in NSFB. However, it appears that the uptake rate of selenite into phytoplankton (k_4) was based on a study using $10\mu\text{g Se/L}$. Is there an additional reason for omitting the Doblin data (or using a combination of the Baines and Doblin data)?

Tetra Tech Response: Se:C ratios, as suggested by previous studies, vary greatly by species (Baines and Fisher, 2001; Doblin et al. 2006). Therefore a Se:C ratio measured in the Delta was considered as the best data available to determine the amount of Se associated with phytoplankton entering the estuary through the Delta. The value of 15.9 (measured by Baines et al. 2004) is well within the range reported by Baines and Fisher (2001) of 0.22 to 30.4 $\mu\text{g/g}$ under the 0.15nM experiment and 0.05 to 217 $\mu\text{g/g}$ under the 0.45 nM experiment. The ratio reported in Doblin et al. (2006) is the atomic ratio (not mass ratio) and a unit conversion from atomic ratio to mass ratio is needed. Based on the molar weight of Se and C, a conversion factor of 78.9/12 was used to convert these atomic ratios. The results for Se:C in $\mu\text{g/g}$ are shown in Table 2-2 of TM-6. These suggest that measured Se:C ratio by Doblin et al. (2006) of 3 to 13.49 (dinoflagellates) $\mu\text{g/g}$, instead of <1 to 4.4. We added this note in the text (p 2-14).

Reviewer's Comment 9: In TM6, the authors note that "Model-predicted selenium concentrations in phytoplankton (in terms of Se:C ratio) were compared to observed values in the seston of the Delta (Baines et al., 2004). The Se:C ratio in phytoplankton is calculated as selenium concentrations associated with phytoplankton ($\mu\text{g/L}$) divided by phytoplankton biomass (in units of carbon, g C/L)." Baines et al. used a C:Chl-a of 28 to estimate a Se:C of 12.05×10^{-6} in the Delta. This was compared to a Se:C of 15.9×10^{-6} in uptake experiments using delta samples. The model reviewed here uses a C:Chl-a of 51 to estimate Se:C in phytoplankton, which would have resulted in a much higher Se:C in the Delta and a less favorable comparison to the experimental Se:C in Baines et al.

It is not clear to me why the carbon to Chl-a ratio was set as 51 mg C to 1 mg Chl-a following Cole and Alpine (1991) instead of 28 mg C to 1 mg Chl-a following Cloern et al 1995 (as was used by Baines et al, 2004). Also Cole and Alpine (1991) is not included in the references and I have not seen that paper. The C:Chl-a ratio has a significant impact on simulated riverine phytoplankton Se since each gram of carbon represents 15.9 μg organic Se.

Tetra Tech Response: The reference should be Alpine and Cloern (1991) and has been corrected in the table. The ratio of 51 is for freshwater phytoplankton and is based on an average of the measured carbon uptake rate. We recognize that this ratio varies in time and space and a wide range is possible. The value of 28 in Cloern et al. (1995) is a modeled value for a single day in June 1993. Ideally, a model of phytoplankton could include the growth-rate impact on the C:Chl a ratio, but this was beyond the scope of the selenium modeling. The text has been modified accordingly (p 2-45).

Reviewer's Comment 10: Boundary Conditions - Seaward Boundary. The seaward boundary for particulate Se is much higher than all other observed data. Other TRC members have voiced concern regarding the use of this boundary condition. This parameter has a large impact on the model outcome and should be reconsidered.

Tetra Tech Response: As a result of discussion at the TRC meeting in April we tested different seaward bound particulate Se concentrations and revised the model seaward boundary concentrations to fit the observed data (~0.8 – 1.0 µg/g) at Golden Gate by Doblin et al. (2006). Figure 3-26 and Figure 3-42 show the comparison with the observed data.

Reviewer's Comment 11: Bioaccumulation in Bivalves: As described above, my estimation of the relative sources of modeled assimilated Se in clams is shown in Tables 2 and 3. These estimates are based on model simulations shown in Figures 4-20 and 4-21 in TM6 and are described in the footnote of these comments. In the model, approximately half of the Se assimilated by bivalves originates in PSP during low flow, while 71 – 82% originates in PSP in high-flow simulations. In a low-flow simulation, the relative sources of assimilated Se in bivalves are estimated as: sediment 23 – 46%, detritus (organic fraction of PSP) 22 – 31% and phytoplankton 29 – 48% (Table 2). In the high flow simulation, the relative sources are estimated as: sediment 36 – 45%, detritus 39 – 45% and phytoplankton 10 – 25% (Table 3: June ,98 & March ,99). This does not agree with my understanding of Se dynamics in NSFB. In most conceptual models, the bioaccumulation of Se in NSFB is driven by phytoplankton. In this model, bioaccumulation is mainly driven by nonliving material entering from the Sacramento Rv. The high level of particulate Se modeled for detritus is particularly out of place. Detritus generally decreases from the confluence of the rivers to San Pablo Bay, but most of the Se in detritus is maintained throughout the estuary in this model. I think there is evidence that detritus is not present at consistently high levels throughout the estuary. Additionally, the assimilation efficiency of 0.8 for particulate organic Se was determined using living phytoplankton -- the assimilation of Se in detritus could be significantly different. Most importantly, as mentioned above, load reduction scenarios do not impact the organic Se fraction of PSP – essentially locking in a highly bioavailable, and flow dependent, parameter in the model.

Tetra Tech Response: Please see response to Comment 3 where this issue is addressed in more detail.

Besides the prior comments, another conceptual model of the bay (Abu Saba and Ogle, 2005) also noted the importance of upstream riverine and Delta sediment inputs: “upstream riverine and Delta sediments and Delta primary productivity are major sources of the suspended particulate selenium”.

The assimilation efficiency of particulate organic selenium has not been determined for nonliving particulate organic selenium; however this form of particulate organic selenium exists in the estuary.

We added these discussions to p2-11, p4-38, and p2-18.

Reviewer's Comment 12: Similarly, the role of sediments in bioaccumulation appears too large in this model. The assimilation efficiencies of sediments are 0.45 and 0.2 for the selenite/selenate and elemental Se fractions. In this model, sediment is a large source of assimilated Se in clams (up to 46 percent of total assimilated). Considering the relatively low assimilation efficiencies of sediment, the clams are assumed to ingest huge amounts of sediment particles. Clams are herbivores and need to consume enough plant material to survive. Many species

of clams have efficient mechanisms to avoid ingesting large volumes of sediment (e.g., pseudofeces or retracting siphon).

Tetra Tech Response: The assimilation efficiencies are based on particulate Se species, regardless of their sources. The reviewer suggests that sediment contribution is too large and that the PSP contribution is also too large. If both are true, this would only suggest that the contribution from phytoplankton is underestimated, based on total observed particulate selenium. However, the phytoplankton concentrations were simulated well by the model. The Se:C ratio used in Delta phytoplankton of 15.9 µg/g and Se:C ratio of 51 were both considered as too high by the reviewer. This would also suggest that the phytoplankton Se is overestimated and not underestimated.

Again we think the role of sediment contribution may be overestimated in the calculations from the reviewer. The bed sediment also contains some organic selenium (Table 2-11 of TM-6) which was taken to be all inorganic by the reviewer. Thus, by adding Se from riverine suspended material and bed sediment, the estimated contribution is actually for inorganic particulate selenium.

The assimilation efficiency has been found to be relatively high for bacteria plankton (possibly present in PSP) (Werner and Hollibaugh, 1993).

If there is quantitative data that clams feed exclusively on living phytoplankton and avoid mineral sediments, we could revise the uptake rates for different sources of particulate selenium.

Reviewer's Comment 13: *The above issues are very important in relation to the simulated swamping effect of the Sacramento River. PSP from this river appears to control the model, yet this parameter is built on a fairly crude estimate of suspended material in NSFB. PSP is a function of a limited number of measurements of total suspended material (a measurement with high temporal variability) and flow rates. The Se contained in PSP is a function of calibration coefficients that fall within a very large range of observed data. The calibration is based on one year of data with limited observations. There is huge room for error in the simulation of PSP yet, because of the complexity and specificity of this model, an air of precision is associated with model predictions. In TM6, this is supported by testing the model using the limited data that falls outside of the calibration data set. The results are promising for a complex model, but level of uncertainty and variation in the model does not support the level of precision conveyed in the conclusions of TM6.*

Tetra Tech Response: We agree that PSP is an important parameter in determining selenium inputs to the bay. However, this is not the only parameter that controls the model output.

PSP as a function of flow is able to capture the range of variation observed in TSM. Observed PSP concentrations at the Rio Vista do not seem very sparse (as shown in Figure 2-12 of TM-6). Alternatively observed PSP concentrations can be used in model inputs, however, this will likely limit the use of the model for future projections with flow changes because PSP is likely to vary with flow.

The model calibration was done using the available data. If more data become available in the future, it will surely help reduce the uncertainties and improve the model simulations. The calibrated values fall within the range of the observed data; the calibrated parameters are the best fit value that can be used to estimate

particulate selenium for future conditions. Although the precision is limited by the large variation in observed data, the standard deviation of the estimated parameters can be used to derive confidence intervals of the model predictions.

We agree there is variation in particulate selenium in riverine inputs, and the variation is likely to be associated with flow and the relative contribution from the two rivers. Therefore different boundary conditions may be used for different flow conditions. For a particular day, the variation seen in particulate selenium in the estuary is not likely due to variation from riverine inputs but rather in-estuary processes given the residence time and this in-estuary process can not be easily captured by a 1-D model. We added some of these discussions to the report (p3-46).

Overall, a model such as this offers a representation of the processes that are understood to be important. It is a tool for analyzing the behavior of selenium in NSFB, and creates a framework for additional data collection. That some features of the data are not fully captured is important to point out, but the solution is to try to improve the existing model and/or calibration. Replacing the model with a simple linear partitioning coefficient does not enhance understanding or serve to guide future monitoring. There is new discussion of this issue under the "Discussions" section (6.7).

Reviewer's Comment 14: Bioaccumulation in Predators - *Figure 3-36 is unclear to me. When discussing the hazard quotient (HQ) of Se exposure to predators, I'm still unclear on your statement that "a large number of conservative assumptions that are incorporated in the estimated HQs and a value slightly greater than 1 does not indicate significant risk." What are the conservative assumptions applied in the estimation of HQ? If the assumption that sturgeon and diving ducks feed exclusively on Corbula is considered conservative, what other NSFB species do you consider as significant food sources for these predators?*

Tetra Tech Response: We consider the assumptions used as conservative because:

1. The diet is assumed to comprise only *Corbula amurensis*, which bioaccumulates selenium most efficiently.
2. The predators were assumed to be present in SF Bay 100% of the time, which may not be true due to migration.
3. The HQs computed were not seasonal or annual averages, but estimated using daily estimates of clam concentrations, which showed clear peaks. Annual average HQs would be lower than the peak HQs that are shown.

The text of this section has been modified to explain what we mean by "conservative assumptions." (p2-23)

Reviewer's Comment 15: Summary and Conclusions: *In summary, I am concerned over the limited review of specific functions in this model. The TRC review process has been lengthy, but has focused on general concepts leading up to the actual (empirical) model. In April 2009, the TRC members did not understand how the model was functioning. The revisions to TM6 did not address several of the specific concern raised at the April meeting.*

Tetra Tech Response: We respectfully disagree with the reviewer's view of the TRC's level of understanding of the model and the extent to which concerns raised by the TRC were addressed in the revised TM-6. The comments received on the revised TM-6 from other TRC members do not concur with the reviewer's opinion.

Reviewer's Comment 16: Summary and Conclusions: *My specific concerns focus on the treatment of particulate Se and the impact of that treatment on bioaccumulation. The model concludes that load reductions would not decrease particulate Se concentrations due to the overwhelming input of the Sacramento River. This concerns me because it is different from our current understanding of Se dynamics in NSFB. When the influx of the Sacramento Rv. is lowest (lowest flow period during low flow year), the Se concentrations in bivalves are the highest. When the influx from the rivers is highest, the bivalves contain significantly lower Se concentrations. In the scientific literature, this is generally related to longer residences times during low-flow and thus greater uptake of Se in phytoplankton. In the model, increased bivalve concentrations during low flow are driven by PSP from Sacramento Rv., while decreased bivalve concentrations during high flow result from higher volumes of sediment diluting the food source of the clams. At least, this was my understanding from talking with the authors.*

In conclusion, I suggest caution in the continued use of this model. The model was highly calibrated to fit a limited set of data. When compared to other limited data sets, the variation and uncertainty is too high to support the level of precision presented in the conclusions of TM6. The drawback of using complex models that are based on very limited data is the potential for overestimating the ability to predict events in the modeled system. On the other hand, the benefit of using simplified models to describe limited data is that the uncertainty of the predictions remains clear. I suggest that you reconsider using the simplified modeling approach presented by Presser and Luoma (2006) to set initial load reduction targets and improve the model described in TM6 with additional data over time.

Tetra Tech Response: We think the contribution of particulates selenium from riverine sources cannot be overlooked, given the large amount of sediment inputs estimated from the Delta by other independent studies. We added this discussion to the text (p 2-11).

Riverine inputs, as estimated, were only a fraction of the total particulate selenium. When riverine inputs are low, the control of dissolved selenium in the estuary can result in changes in particulate selenium concentrations (Figure 5-4 of updated TM-6). Given the right combination of conditions (low flow-> low riverine input and high Chl a concentration) the changes in dissolved selenium will result in uptake into particulate selenium and these transformations can be significant.

We are a little unclear about the comment that the current understanding of selenium dynamics in NSFB is different from the results.

The model provides temporal and spatial variation of simulated selenium in particulates and bivalves that has not been achieved by a simple partitioning model. It also provides spatial and temporal variation of loads going into the estuary. Moreover, it gives consideration of speciation effects from different sources of selenium and the uptake of selenium by phytoplankton and bivalves depends on simulated selenium concentrations by species. Although limited by data in some areas, the model uses the best information available today and assembles the most current scientific understanding of selenium biogeochemistry

in this estuary. Ultimately it is up to the Water Board to decide what model to use. We think the model described in TM-6, with its assumptions clearly stated is sufficiently robust to be used as part of the decision-making process for the selenium TMDL.

A.5.4.3 Comments on the June 19 2009 draft of Technical Memorandum 6, Samuel N. Luoma, July 6, 2009

Tetra Tech responses are inserted in this color and font.

Reviewer's General Comment: *The changes in the report, overall, have really improved its transparency and understandability. The improved executive summary does an excellent job of explaining the calibration, evaluation and predictive modes in which the model is developed and employed. The addition of moderated language and detail about predictions, as well as the discussion of limitations and assumptions is an important improvement. Discussion of sensitivity to assumptions about the Sacto River, under current discharge conditions, and the call for more data in this regard is also quite valuable. In the report, the section on boundary conditions is another very important addition that adds greatly to the clarity of the document, as does Figure 2-16. As I will note below, I do not believe that the chosen boundary conditions represent the Bay's true boundary conditions, but because they are well explained they are acceptable as long as they are not mis-used (see below).*

The advanced simulations under different boundary conditions represent a great deal of work and are also quite valuable. It was important to show the degree to which dissolved and particulate Se are most sensitive to riverine input parameters and that particulate selenium concentrations are sensitive to selenium content on particulate material at the head of the estuary. The details of the simulations were insightful. The scenarios are also informative and more robust than in earlier reports.

I really only have one serious objection to the present document. It boils down to Scenario 10 and it is serious because it represents a long standing point of contention in the ongoing disputes about Se in the Bay. One of the bulleted conclusions seems to build from this and it has serious implications, if taken to an extreme, for the TMDL. If I understand the model correctly, Scenario 10 uses the particulate Se boundary conditions specified earlier in the report. These use particulate Se data from Doblin for the landward concentrations taken from stations that are, in fact, within the tidal influence of the Bay (i.e. Bay particulates, not river particulates during a time when the Bay was more contaminated than it is now). What I read scenario 10 to say is that if point source loads are removed and local tributary loads are removed and the SJR dissolved Se drops to 0.2 ug/L there will still be no change in Se concentrations in the bivalves? What is not stated, if I am correct about the boundary conditions, is that conclusion is valid only if particulate Se stays at 1999 levels. Doesn't this assume that the drop in dissolved Se that the model predicts under these circumstances,

will not be accompanied by a decrease in particulate Se. In fact, under these conditions shouldn't particulate Se at the riverine boundary be almost the particulate Se in the Sacramento River (for which we have no data, but it surely is among the lowest of the Doblin numbers, not the average – about 0.05 ug/g). It is a self-fulfilling prophesy that the bivalve Se will not go down as long as particulate

Se does not go down. With a Kd range of 10^3 to 10^4 in every instance where particulates and dissolved Se it seems logical to assume that a drop in dissolved Se will result in some effect on particulate Se in the long run. The way Scenario 10 is presented it allows the politically volatile and, in my view, illogical conclusion that Se inputs to the Bay make no difference to bivalves; in essence the implication is that the contamination of the Bay is the fault of *C. amurensis*, despite the fact that the contamination in predators preceded the invasion of this bivalve. In fact one of your conclusions still hints at this (see below). This of course could easily lead to the further conclusion that adding Se back to the Bay will have no effect on contamination of the food web. If that is the conclusion of the model, then I think it should be stated clearly so it can be debated. But that conclusion is purely a function of the boundary conditions of the model that I just stated, unless I completely misunderstand them, which I don't believe is true. This report is a vast improvement over earlier editions and is becoming quite an impressive document. But to finish with a conclusion that goes back to the same old arguments with the same old origins seems unconstructive.

Tetra Tech Response: Scenario 10 when looked at closely resulted in some changes in particulate selenium concentrations and Se concentrations in bivalves. When point source loads are removed and the SJR loads are reduced to 0.2 $\mu\text{g/L}$, the particulate selenium concentrations decreased by 0.05 $\mu\text{g/g}$ and Se concentrations in bivalves decreased by 1.2 $\mu\text{g/g}$. Gridlines were added to Figure 5-4 and Figure 5-5 of TM6 to show the difference among the scenarios. It is possible to run a scenario with a much lower value of particulate Se as the boundary condition at the riverine end than observed in 1999. Indeed, scenarios with a wide range of boundary conditions were presented in Figure 4-16.

We can discuss with the TRC what this boundary condition could be and re-run the simulation. Note that there are no data that could be used to define this condition. The current values were used because the Doblin et al. analysis did not show values at Rio Vista dropping very low even when the salinity was low (suggestive of conditions with minimal bay influence).

Reviewer's Comment 1: Minor points and a couple points of interest: There are many scenarios that could be run with the model. They do not have to be done now, but it would be interesting to include that in future needs. For example, what happens when change proportional contributions of two rivers to the Bay by greatly cutting Sacto inputs and using values from Vernalis as if no diversions? Halve Sacto and triple SJR simultaneously = worst case but maybe a Peripheral Canal case.

Tetra Tech Response: We ran a scenario with increased flow to Vernalis flow without cutting Sacramento River flow and it appears to result in changes in particulate selenium (as in TM6). We tested a scenario of half Sacramento and triple SJR (see Figure 1 below). Additional scenarios are planned to be run in a separate TM (TM-7), once there is agreement on the approach used in TM-6.

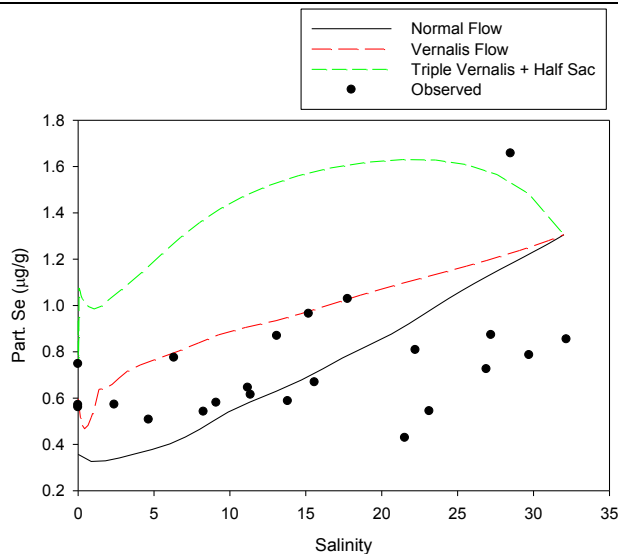


Figure A.5-1 Simulated particulate selenium under the scenarios of increasing SJR flow input to Vernalis River flow and increasing SJR flow to triple Vernalis flow and half Sacramento River.

Reviewer's Comment 2: Page xviii, end of paragraph 1 seems an important sentence but it is confusing. Paragraph 2 is very important to future water management strategies. Be sure these are clearly stated.

Tetra Tech Response: The sentence at the end of paragraph 1 was not well-worded. Here is what we now say: "The finding that particulate concentrations are relatively insensitive to decreases in dissolved selenium loads particularly during the high flow season, is significant from the standpoint of the TMDL process."

Reviewer's Comment 3: As discussed above, the bulleted statement: "The current assessment of risk to predator species in the bay from selenium uptake is largely a result of the presence of *Corbula amurensis*, despite the two-decade long efforts to control non-point sources in the Central Valley and point sources in the bay." What does this mean? Surely you are not implying that there is no effect from source inputs to the Bay...that what we have always seen is background concentrations in *C. amurensis*? How does this square with declining concentrations over recent years? With the fact that predators were contaminated to a similar degree pre-invasion of *C. amurensis*. How about: "The risks to predator species in the bay from selenium uptake are very sensitive to changes in particulate concentrations because of the presence of *C. amurensis*, an organism that bioaccumulates Se strongly when small changes in particulate concentrations occur and passes that Se up the benthic food web".

Tetra Tech Response: This means the presence of *Corbula* is an important part of the problem of selenium bioconcentration in the food chain, relative to other species of bivalves. Looking at recent bivalve data (after the June 19 version of TM-6 was prepared), we agree with the reviewer's comment that selenium concentrations in bivalves may be decreasing in recent years, although they show large inter-annual variations, and the model is predicting that change well. In the revised executive summary, the sentence referenced above has been modified as suggested.

Reviewer's Comment 4: *Doblin defines the Delta as "sites above Chipps Island". The most landward site was Rio Vista (I was on many of these cruises). These were all sites within the tidal influence of the Bay and therefore the particulate material there originates from the Bay and is strongly influenced by Se-contaminated Suisun Bay. Thus this boundary condition is not a riverine endmember but is river particulates mixed with Bay particulates, similar to the RMP "Sacramento River" site. In the end, in the model, Se concentrations on particulates were still kept constant and the boundary condition was derived from a Bay-influenced location samples by Doblin. The effect is to overestimate the Sacramento River boundary concentration and probably underestimate the SJR boundary compared to what is the reality. Pp. 2-43. Similarly the seawater boundary condition is a constant that is from a location strongly influenced by the Bay. This is more complex and probably less important to the TMDL, however. There is a great need for more data collection from the real river endmembers and from the coastal endmember.*

Tetra Tech Response: Without particulate selenium data from the real end member (Vernalis or Freeport), we can only use data from Delta as inputs to the Bay. We agree some of the Rio Vista particulate selenium data may reflect Bay influence or mixed with the San Joaquin River, but at least should be dominantly Sacramento River input during high flow (as estimated using DAYFLOW values and salinity measurements at the time of Se sampling). If we assume particulate selenium measured at Rio Vista during high flow reflects inputs from Sacramento River well, then the load from Sacramento River during high flow should be estimated reasonably well. We used the Delta data to derive Kd values for the SJR input. Although the SJR input may be underestimated, the Delta's effects of the SJR input need to be considered as well. After all, SJR enters the Bay through the Delta. We revised the text (p2-43) that particulate selenium from Rio Vista and Delta sampling stations may have bay influence.

Reviewer's Comment 5: *P3-32. The conclusions about predictions of dissolved Se should state something like: "the model captured the central tendencies of concentration of Se in the estuary as well as seasonal variations. But many of the highest peak concentrations were not well predicted, suggesting a cause that was outside of the conditions and/or assumptions set for the model." This is captured in a phrase on p. 3-37, but the longer explanation on p. 3-32 should be just as direct. Similarly, in Fig. 3-40 and 3-41, the model does a very good job of capturing the central tendency of the particulate Se data, but it does not capture some of the higher concentrations. Fig. 3-41 shows a better fit, but it should as it builds from two boundary conditions defined by the average Se on particulate material; nevertheless, the two highest data points are not predicted by the model in these transects. When Doblin et al sampled particulates at two stations through time there were a number of instances of concentrations elevated above the central tendency of the data. I think some point must be made of this weakness in the model, if it is to be used into the future. Indeed the conclusions on pg 3-55 is correct: "the model represents key features".. But a balanced report would follow that with a statement about the difficulty of predicting episodic increases in Se concentration. The model somehow does not capture their source. I think you could also add that "these features probably lie in the complexity of inputs from the rivers and interactions in the Delta that are poorly known." Personally, I think it is likely that there are times when more SJR water enters the Bay than the model assumes. For example, an under-prediction could result from higher Se in the SJR*

in the early years and a lower Delta capturing efficiency when the barriers are in or when the ratio of the two river discharges is at one extreme or the other. I do not know how one would incorporate that into a model...we just don't know enough. But it is important to be frank about, in case these periodic changes are biologically important.

Tetra Tech Response: We thank the reviewer for pointing out these caveats. We revised the discussion on P3-32 to say that some of the high concentrations are not captured by the model and this may be due to variations in load inputs that are not represented well by the model, and incorporated the discussion above.

With respect to the higher concentrations in Figure 3-40 and 3-41, some of these may also be due to in-situ processes of sediment suspension (PSe0) or variations in phytoplankton concentrations or species (POrgSe). This has also been added to the report.

Reviewer's Comment 6: *In describing Fig. 3-29, the model predicts an increasing concentration of Se in clams between the Carquinez Straits to the Golden Gate. There is only data from one station in San Pablo Bay but those data do not support this (and that is consistently the case in later data from that site). Otherwise the agreement is good. A more direct statement about the difference between prediction and observation would help, if only to emphasize that the San Pablo to the Golden Gate area might need more information. What was the outcome of the study you all did of Se in bivalves? Did such a geographic trend appear? Why isn't that data mentioned? Would be a good way to determine if this area that the model has trouble with or is just an anomaly resulting from the location of the USGS San Pablo Bay station.*

Tetra Tech Response: The trend appears to be evident that bivalve selenium concentrations increase from Carquinez Strait to San Pablo Bay (although there is only 1 station in San Pablo Bay). Data from Stewart (Stewart, R. 2007. Within Delta Conveyance: Environmental Water Quality Issues. CALFED Science Program Workshop Summary. Science Issues Relating to Delta Conveyance Infrastructure: Through Delta Options. September 11, 2007) showed an increasing trend of selenium concentrations towards higher salinity, although the data only extend to San Pablo Bay, not to Central Bay. This only indicates more data in the Central Bay are needed. As particulate selenium concentrations seem to increase toward central bay, there is no reason to reject the hypothesis that selenium concentrations in bivalves also increased towards that direction. The report is revised to note (on page 3-38) the limited data now used for the model comparison (temporal and spatial extent) and the need for comparisons with additional data.

The clam data collected by us are shown below (and compared to published data) (Figures 2 and 3). These were for a single point in time (late 2008) compared to other data used in the model evaluation from the 1990's. A comparison of the model with these data as well as others in the interim period (i.e., between 2000 and 2008) can be presented when such data become available.

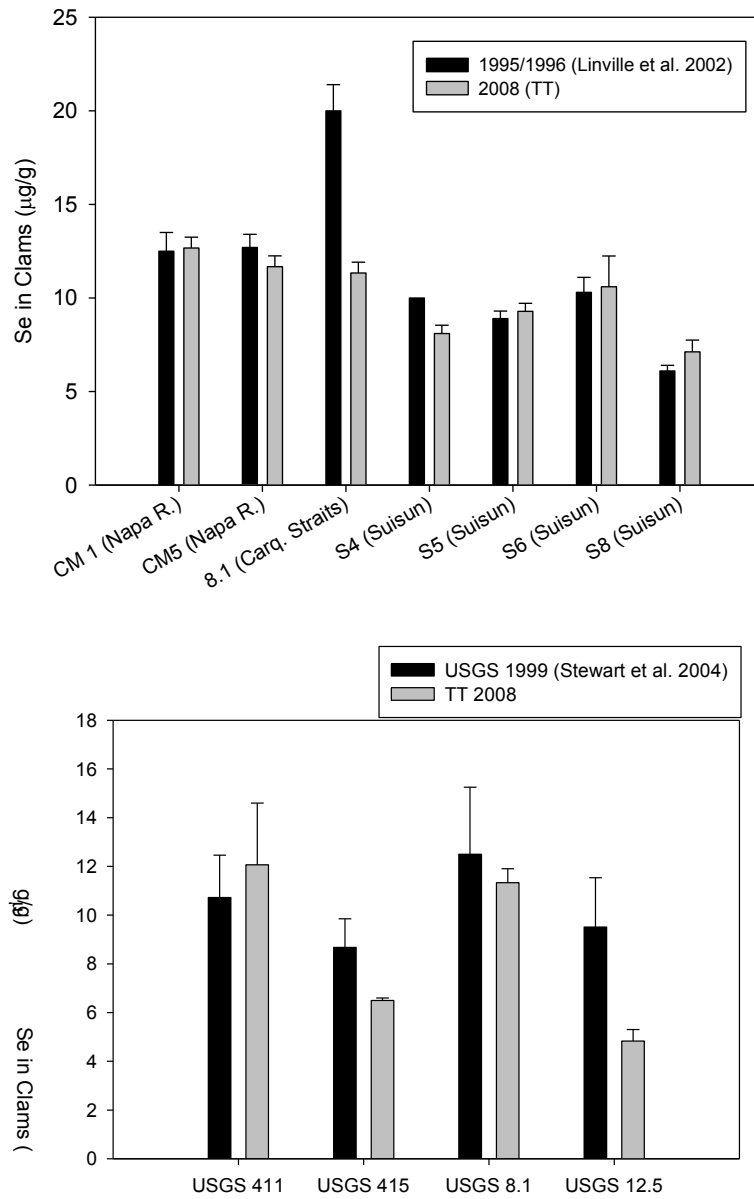


Figure A.5-2 November 2008 clam sampling by Tetra Tech, using sampling and analysis protocols identical to those of USGS, compared to published values.

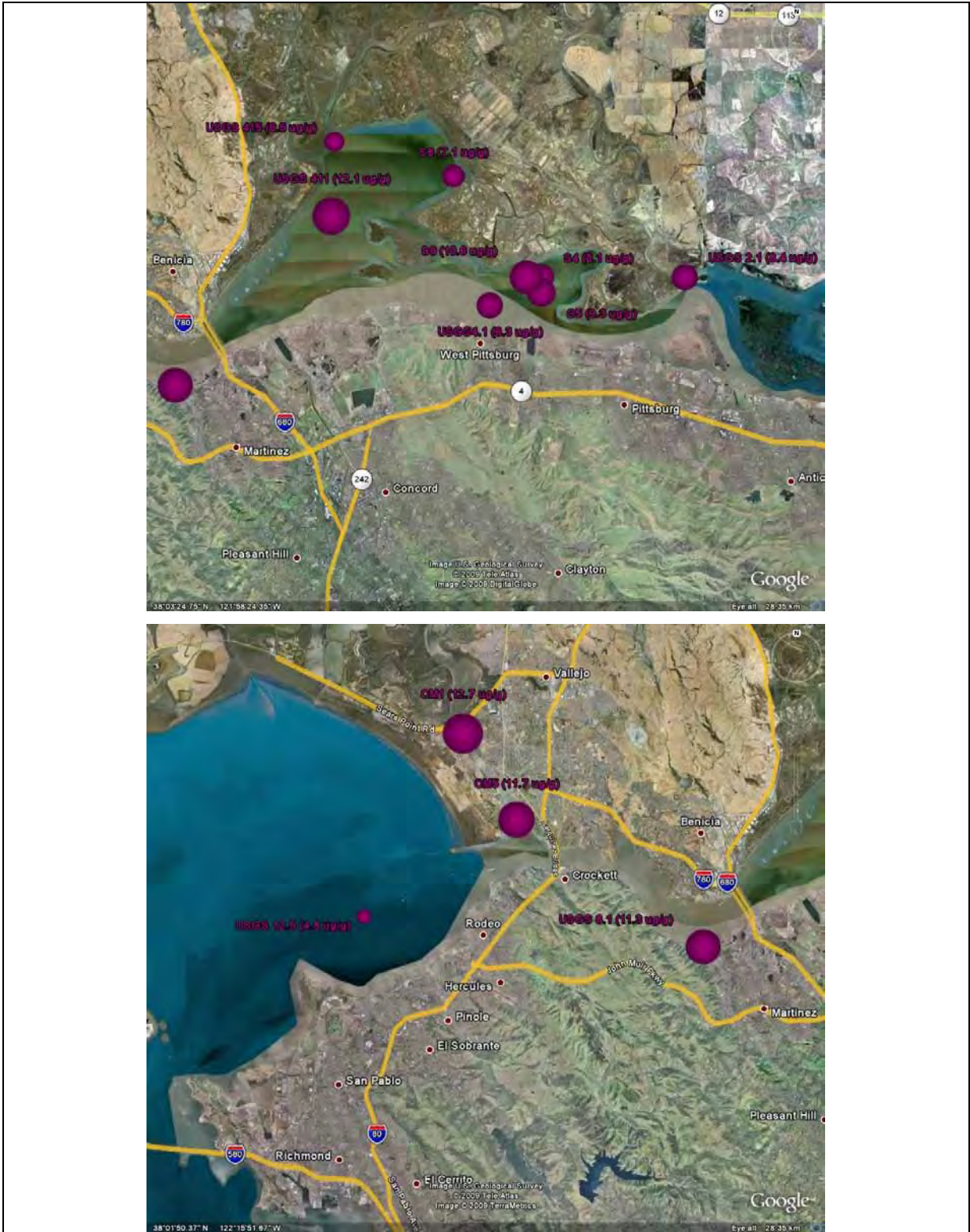


Figure A.5-3 Map of November 2008 clam sampling by Tetra Tech, using sampling and analysis protocols identical to those of USGS.

Reviewer's Comment 7: *I was especially interested in the uptake rate/mineralization rate discussion and testing of this against field data. It was a nice discussion. The rate of Se uptake by phytoplankton was a source of some discussion by the review committee. On page 2-9 you make an insightful statement that I believe helps resolves this when you state both the rates and the concentrations at which those were determined. As the authors know, the rates estimated by Baines and by Reidel are rates, not rate constants. Rate of uptake is a function of Se concentration, of course; the contentious question being to what concentration does Se concentration accumulate in phytoplankton if Se in the water increases. The rate constant times the concentration gives the absolute rate at any concentration, assuming the relationship between the two can be defined mathematically (which, of course is a subject of some discussion if one looks at the shape of the Baines & Fisher M-M curve). But one could also estimate a rate constant for Se uptake by plotting the rates of uptake found by Baines' study and the one found by Reidel against the average concentration in those two studies (I know, only two data points). The slope is the rate constant of uptake (we call it K_u) in ug/g/d per ug/L or L/g/d. The rate constant is $(2/0.3)/.02/10 = 0.013$. Interestingly this is very similar (within the same order of magnitude) to the K_u (rate constant of uptake) by animals for selenite. That helps us address the discussion of how or if Se uptake by phytoplankton changes as concentration changes. The differences between the studies of Reidel and Baines is direct evidence that there is indeed a change in Se taken up over this concentration range, if one takes both studies as equally valid. In that case, how much Se bioaccumulation would be expected between Baines' range of concentrations? At a K_u of 0.013, a 10 fold increase in concentration would result in a (10×0.013) thirteen percent increase in Se uptake. Not too different from what Steve and Nick suggest. Just a thought.*

Tetra Tech Response: This is a very good point, and an interesting point of discussion with the TRC. Does this argue against the use of a direct linear relationship between dissolved and phytoplankton concentrations?

Reviewer's General Comment: *Overall, I would say an excellent report, but it still has a few kinks that could unnecessarily ignite emotions. I very much respect the serious and thorough effort to address the quite knotty problems raised by the comments. By participating in the building of this model we all have learned a great deal about Se in the Bay that can be constructively applied to the TMDL. I believe there is much to recommend an ongoing use of this model as the TMDL is implemented and, hopefully, a monitoring program is implemented.*

A5.5 CONFERENCE CALL WITH TRC TO DISCUSS COMMENTS AND RESPONSES, OCTOBER 26, 2009.

A final conference call with the TRC members was conducted on October 26, 2009 to discuss the findings from the review process and to present a revised version of TM6 that incorporate the responses to the additional comments received from TRC (see Item 4 above). The following points, prepared by the Water Board, provide a summary of the understanding of the outcome of the discussions and recommendations derived from the TRC process.

- The model is a legitimate tool to use in evaluating scenarios and can be constructively applied to the TMDL development process.

- The technical memorandum reflects the current state of knowledge of biogeochemical transformations of selenium and processes leading to selenium bioaccumulation in the North Bay.
- All available data have been used in setting-up, testing, calibration and validation of the model.
- The scenarios evaluated in the model allow us to examine model performance. Additional scenarios can be evaluated using this model to support a linkage analysis and to examine the potential for recovery of the system given different scenarios.
- The revised report demonstrates that the model is robust, provides details of the underlying assumptions built into the model, and identifies potential limitations of the model and the available data.

The outcome of this final meeting with the TRC was a general consensus on these summary points. However, the TRC members requested clarification of two key points:

- The need to explicitly state the importance as well as the uncertainty associated with the values selected to represent the particulate selenium concentrations at the Sacramento River, which represents one of the boundary conditions.
- The need for a more focused data collection efforts and laboratory studies to better characterize the transformations between different forms of selenium.

In this document, the *Draft Final Technical Memorandum 6: Application of ECoS3 for Simulation of Selenium Fate and Transport in North San Francisco Bay*, the Executive Summary and Section 6 (Discussion) were revised in response to the comments received from the TRC during this teleconference and subsequent e-mail exchanges to highlight both the importance and the uncertainties in riverine and ocean boundary conditions and their effect on the model results and the conclusions. It is noted in the revised document that future model development may seek to address some of the shortcomings of the modeling presented in this report, but such model development must be preceded by an adequate data collection program.

A5.6 APPENDIX REFERENCES

Tetra Tech, Inc. 2008. Technical Memorandum #8. Recommendations for the Technical Review Committee. April 2008. Report to the Regional Water Quality Control Board, San Francisco Bay Region.

RWQCB, 2007. Project Plan: North San Francisco Bay Selenium TMDL. July 2007.

APPENDIX 6: SUPPORTING CALCULATIONS FOR THE AUGUST 12, 2009 COMMENTS FROM REGINA LINVILLE (APPENDIX 5, PAGE A.5-26)

Table A.6-1
Example Calculation

Table 1: Example Calculation

Description	Value	Units	Source
Flow (avg Nov 1999)	3.4×10^{10}	l/d	DAYFLOW
PSP	0.010	g/l	Estimate
Elemental Se in PSP (Se OPSP)	0.1	ug/g	Table 3-3 of TM6
Selenite/Selenate in PSP (Se (IV + VI))	0.202	ug/g	Table 3-3 of TM6
Organic Se PSP (Org Se-II)	0.166	ug/g	Table 3-3 of TM6
Organic Se in Phyto	15.9	ug/g C	Table 3-2 of TM6
Chla	1.2	ug/L	(reflects delta at low flow 1999, see Fig 2 of Doblin)
C:Chla	51 mg C/ mg Chla	mg C	Table 3-2 of TM6
Phytoplankton	0.06	mg C/L	$0.0012 \text{ mg Chla/L} * 51 \text{ mg C/mg Chla}$
Loads			
Elemental Se in PSP (Se OPSP)	34	g Se/d	$\text{flow (l/d)} * \text{PSP (g/l)} * \text{Se OPSP PSP (ug/g)} = \text{ug Se/d}$
Selenite/Selenate in PSP (Se (IV + VI))	68	g Se/d	$\text{flow (l/d)} * \text{PSP (g/l)} * \text{Se (IV + VI) PSP (ug/g)} = \text{ug/d}$
Organic Se PSP (Org Se-II)	56	g Se/d	$\text{flow (l/d)} * \text{PSP (g/l)} * \text{Org Se-II PSP (ug/g)} = \text{ug/d}$
Total Se on PSP	159	g Se/d	Se OPSP PSP + Se (IV + VI) PSP + Org Se-II PSP g Se/d
Organic Se in Phyto	33	g Se/d	$\text{flow (l/d)} * \text{C g/L} * 15.9 \text{ ug Se/g C} = \text{ug/d}$

Table A.6-2
Relative Sources of Selenium Assimilated into Bivalves Based on Low-flow Model Simulation in Figure 4-20*

Table 2: Relative sources of selenium assimilated into bivalves based on low-flow model simulations in Figure 4-20 †§

Salinity	Bioavailable Particulate Se				Bioavailable Particulate Organic Se			Bioavailable Se by Model Compartment		
	Total Particulate Bioavailable Se (Bio P Se) ug/g	% of all Bio P Se			Organic Particulate Bioavailable Se (Bio P Se (-II)) ug/g	% of Bio P Se (-II)		% of all Bio P Se		
		Sedi ^{††}	Detritus	Phyto		PSP	Phyto	PSP	BESP	Phyto
	%	%	%	%	%	%	%	%	%	%
0	0.139	46%	25%	29%	0.075	46%	54%	45%	26%	29%
2.5	0.128	46%	22%	31%	0.069	42%	58%	41%	28%	31%
5	0.163	36%	25%	39%	0.104	39%	61%	45%	16%	39%
10	0.284	29%	26%	45%	0.203	37%	63%	48%	7%	45%
15	0.392	26%	29%	45%	0.288	39%	61%	52%	3%	45%
20	0.516	24%	28%	48%	0.392	37%	63%	51%	1%	48%
25	0.662	23%	28%	48%	0.507	37%	63%	51%	0%	48%
30	0.755	25%	31%	45%	0.566	41%	59%	55%	0%	45%

† Using parameters for Se speciation in PSP and assimilation efficiency factors from the model (AE = 0.2, 0.45 and 0.8 for elemental Se, Se IV/VI, and organic Se, see tables 4 & 5).

§ Estimations of organic Se in PSP are likely artificially elevated at higher salinities since selenite is added to PSP as it travels through the estuary.

†† Sediment is all inorganic selenium (from PSP and BESP)

Table A.6-3
Relative Sources of Selenium Assimilated into Bivalves on Simulation for Carquinez Strait in Figure 4-21*

Table 3: Relative sources of selenium assimilated into bivalves based on simulations for Carquinez Strait in Figure 4-21 †

Date	Bioavailable Particulate Se				Bioavailable Particulate Organic Se			Bioavailable Se by Model Compartment		
	Total Particulate Bioavailable Se (Bio P Se) ug/g	% of all Bio P Se			Organic Particulate Bioavailable Se (Bio P Se (-II)) ug/g	% of Bio P Se (-II)		% of all Bio P Se		
		Sedi ^{††}	Detritus	Phyto		PSP	Phyto	PSP	BESP	Phyto
	%	%	%	%	%	%	%	%	%	%
Jun-98	0.222	36%	39%	25%	0.142	61%	39%	71%	4%	25%
Nov-98	0.242	35%	38%	26%	0.156	59%	41%	69%	4%	26%
Mar-99	0.159	45%	45%	10%	0.088	82%	18%	82%	8%	10%
Nov-99	0.448	25%	28%	46%	0.335	38%	62%	51%	2%	46%

† Using parameters for Se speciation in PSP and assimilation efficiency factors from the model (AE = 0.2, 0.45 and 0.8 for elemental Se, Se IV/VI, and organic Se, see tables 4 & 5).

†† Sediment is all inorganic selenium (from PSP and BESP)

**Table A.6-4
Interpreted Data from Figure 4-20 and 4-21 in TM6**

Table 4: Interpreted Data from Fig 4-20 & 4-21 in TM6

Data interpreted from Fig 4-20. Nov 1999 Particulate selenium through estuary

Salinity	PSP*				BESP	Phyto
	Total Se	Elemental	Selenite/ selenate	Organic	Total Se	Total Se
	ug/g				ug/g	ug/g
0	0.12	0.025	0.052	0.043	0.18	0.05
2.5	0.10	0.021	0.043	0.036	0.18	0.05
5	0.14	0.029	0.060	0.050	0.13	0.08
10	0.26	0.055	0.112	0.094	0.10	0.16
15	0.39	0.082	0.168	0.140	0.06	0.22
20	0.50	0.105	0.215	0.180	0.03	0.31
25	0.65	0.137	0.280	0.234	0.01	0.40
30	0.80	0.168	0.344	0.288	0.00	0.42

PSP*				BESP	Phyto
Total Se	Elemental	Selenite/ selenate	Organic	Total Se	Total Se
ug/L				ug/L	ug/L
0.0045	0.0009	0.0019	0.0016	0.007	0.0019
0.0044	0.0009	0.0019	0.0016	0.0078	0.0021
0.0042	0.0009	0.0018	0.0015	0.005	0.0022
0.0043	0.0009	0.0018	0.0015	0.0018	0.0024
0.0043	0.0009	0.0018	0.0015	0.0008	0.0026
0.0043	0.0009	0.0018	0.0015	0.0002	0.0027
0.0045	0.0009	0.0019	0.0016	0.0001	0.0026
0.0046	0.0010	0.0020	0.0017	0	0.0025

Data interpreted from Fig 4-21. Particulate selenium at Carquinez Strait

Date	PSP*				BESP	Phyto
	Total Se	Elemental	Selenite/ selenate	Organic	Total Se	Total Se
	ug/g				ug/g	ug/g
Jun-98	0.3	0.063	0.129	0.108	0.045	0.07
Nov-98	0.32	0.067	0.138	0.115	0.05	0.08
Mar-99	0.25	0.053	0.108	0.090	0.06	0.02
Nov-99	0.44	0.092	0.189	0.158	0.05	0.26

PSP*				BESP	Phyto
Total Se	Elemental	Selenite/ selenate	Organic	Total Se	Total Se
ug/L				ug/L	ug/L
0.0170	0.0036	0.0073	0.0061	0.0015	0.0030
0.0065	0.0014	0.0028	0.0023	0.0015	0.0040
0.0220	0.0046	0.0095	0.0079	0.0090	0.0020
0.0045	0.0009	0.0019	0.0016	0.0008	0.0025

* PSP speciation estimated from parameters in Table 3-3 of TM6 (as percentages of total Se in PSP)

Se Species in PSP	ug/g	% of Total PSP Se
Elemental	0.1	21%
Selenite/ selenate	0.202	43%
Organic	0.166	36%
Total Se	0.468	

Table A.6-5
Calculations of Bioavailability Se from Figures 4-20 and 4-21 in TM6

Table 5: Calculations of Bioavailable Se from Figures 4-20 & 4-21 in TM6
 (Bioavailability based on modle AE's: 0.2 elemental Se; 0.45 selenite/ selenate; 0.8 Organic Se)

Bioavailable Se based on Figure 4-20 in TM6 shown as ug/g
 (Particulate Se simulated for low-flow)

Salinity	Total Particulate Bioavail Se (Bio P Se)	Bioavailable Se by Model Compartment						Bioavailable Se by Partical Type					
		PSP		BESP		Phyto		Sediment (all inorganic Se)		Detritus (organic fraction of PSP)		Phytoplankton	
		Bioavail Se	% of Bio P Se	Bioavail Se	% of Bio P Se	Bioavail Se	% of Bio P Se	Bioavail Se	% of Bio P Se	Bioavail Se	% of Bio P Se	Bioavail Se	% of Bio P Se
0	0.139	0.063	45%	0.036	26%	0.040	29%	0.064	46%	0.035	25%	0.040	29%
2.5	0.128	0.052	41%	0.036	28%	0.040	31%	0.060	46%	0.029	22%	0.040	31%
5	0.163	0.073	45%	0.026	16%	0.064	39%	0.059	36%	0.040	25%	0.064	39%
10	0.284	0.136	48%	0.020	7%	0.128	45%	0.081	29%	0.075	26%	0.128	45%
15	0.392	0.204	52%	0.012	3%	0.176	45%	0.104	26%	0.112	29%	0.176	45%
20	0.516	0.262	51%	0.006	1%	0.248	48%	0.124	24%	0.144	28%	0.248	48%
25	0.662	0.340	51%	0.002	0%	0.320	48%	0.155	23%	0.187	28%	0.320	48%
30	0.755	0.419	55%	0.000	0%	0.336	45%	0.188	25%	0.230	31%	0.336	45%

Table 5 (cont'd): Calculations of Bioavailable Se from Figures 4-20 & 4-21 in TM6
 (Bioavailability based on modle AE's: 0.2 elemental Se; 0.45 selenite/ selenate; 0.8 Organic Se)

Bioavailable Se based on Figure 4-20 in TM6 shown as ug/L
 (Particulate Se simulated for low-flow)

Salinity	Total Particulate Bioavail Se (Bio P Se)	Bioavailable Se by Model Compartment						Bioavailable Se by Partical Type					
		PSP		BESP		Phyto		Sediment (all inorganic Se)		Detritus (organic fraction of PSP)		Phytoplankton	
		Bioavail Se	% of Bio P Se	Bioavail Se	% of Bio P Se	Bioavail Se	% of Bio P Se	Bioavail Se	% of Bio P Se	Bioavail Se	% of Bio P Se	Bioavail Se	% of Bio P Se
0	0.0053	0.002	45%	0.001	27%	0.00152	29%	0.002	47%	0.0013	25%	0.0015	29%
2.5	0.0055	0.002	42%	0.002	28%	0.00168	30%	0.003	47%	0.0013	23%	0.0017	30%
5	0.0050	0.002	44%	0.001	20%	0.00176	35%	0.002	40%	0.0012	24%	0.0018	35%
10	0.0045	0.002	50%	0.000	8%	0.00192	42%	0.001	30%	0.0012	27%	0.0019	42%
15	0.0045	0.002	50%	0.000	4%	0.00208	46%	0.001	26%	0.0012	28%	0.0021	46%
20	0.0045	0.002	51%	0.000	1%	0.00216	49%	0.001	24%	0.0012	28%	0.0022	49%
25	0.0045	0.002	53%	0.000	0%	0.00208	47%	0.001	24%	0.0013	29%	0.0021	47%
30	0.0044	0.002	55%	0.000	0%	0.00200	45%	0.001	25%	0.0013	30%	0.0020	45%

Table A.6-5 (continued)
Calculations of Bioavailability Se from Figures 4-20 and 4-21 in TM6

Table 5 (cont'd): Calculations of Bioavailable Se from Figures 4-20 & 4-21 in TM6
 (Bioavailability based on model AE's: 0.2 elemental Se; 0.45 selenite/ selenate; 0.8 Organic Se)

Bioavailable Se based on Figure 4-21 in TM6 shown as ug/g
 (Particulate Se simulated at Carquinez Strait)

Date	Bioavailable Se by Model Compartment						Bioavailable Se by Partial Type					
	PSP		BESP		Phyto		Sediment (all inorganic Se)		Detritus (organic fraction of PSP)		Phytoplankton	
	Bioavail Se	% of Bio P Se	Bioavail Se	% of Bio P Se	Bioavail Se	% of Bio P Se	Bioavail Se	% of Bio P Se	Bioavail Se	% of Bio P Se	Bioavail Se	% of Bio P Se
Jun-98	0.222	71%	0.009	4%	0.056	25%	0.080	36%	0.086	39%	0.056	25%
Nov-98	0.242	69%	0.010	4%	0.064	26%	0.085	35%	0.092	38%	0.064	26%
Mar-99	0.159	82%	0.012	8%	0.016	10%	0.071	45%	0.072	45%	0.016	10%
Nov-99	0.448	51%	0.010	2%	0.208	46%	0.114	25%	0.127	28%	0.208	46%

Table 5 (cont'd): Calculations of Bioavailable Se from Figures 4-20 & 4-21 in TM6
 (Bioavailability based on model AE's: 0.2 elemental Se; 0.45 selenite/ selenate; 0.8 Organic Se)

Bioavailable Se based on Figure 4-21 in TM6 shown as ug/L
 (Particulate Se simulated at Carquinez Strait)

Date	Bioavailable Se by Model Compartment						Bioavailable Se by Partial Type					
	PSP		BESP		Phyto		Sediment (all inorganic Se)		Detritus (organic fraction of PSP)		Phytoplankton	
	Bioavail Se	% of Bio P Se	Bioavail Se	% of Bio P Se	Bioavail Se	% of Bio P Se	Bioavail Se	% of Bio P Se	Bioavail Se	% of Bio P Se	Bioavail Se	% of Bio P Se
Jun-98	0.0116	77%	0.000	3%	0.00240	21%	0.004	37%	0.0049	42%	0.0024	21%
Nov-98	0.0069	49%	0.000	4%	0.00320	46%	0.002	27%	0.0019	27%	0.0032	46%
Mar-99	0.0149	77%	0.002	12%	0.00160	11%	0.007	47%	0.0063	42%	0.0016	11%
Nov-99	0.0045	52%	0.000	4%	0.00200	44%	0.001	27%	0.0013	29%	0.0020	44%

Table A.6-5 (continued)
Calculations of Bioavailability Se from Figures 4-20 and 4-21 in TM6

Table 5 (cont'd): Calculations of Bioavailable Se from Figures 4-20 & 4-21 in TM6
 (Bioavailability based on mode AE's: 0.2 elemental Se; 0.45 selenite/ selenate; 0.8 Organic Se)

Bioavailable Se based on Figure 4-20 in TM6 shown as ug/g
 (Particulate Se simulated for low-flow)

Salinity	Bioavailable Se from PSP								Bioavailable Particulate Organic Se					
	Total Particulate Bioavail Se (Bio P Se)	PSP							Particulate Organic Se					
		Total	Elemental		Selenite / Selenate		Org Se		All Particulate Organic Se (Bio Org Se)	PSP Org Se		Phyto Org Se		
		Bioavail Se	Bioavail Se	% of Bio PSP	Bioavail Se	% of Bio PSP	Bioavail Se	% of Bio PSP		Bioavail Se	% of Bio Org Se	Bioavail Se	% of Bio Org Se	
ug/g	ug/g	ug/g	%	ug/g	%	ug/g	%	ug/g	ug/g	%	ug/g	%		
0	0.139	0.063	0.005	8%	0.023	37%	0.035	55%	0.075	0.035	46%	0.040	54%	
2.5	0.128	0.052	0.004	8%	0.019	37%	0.029	55%	0.069	0.029	42%	0.040	58%	
5	0.163	0.073	0.006	8%	0.027	37%	0.040	55%	0.104	0.040	39%	0.064	61%	
10	0.284	0.136	0.011	8%	0.050	37%	0.075	55%	0.203	0.075	37%	0.128	63%	
15	0.392	0.204	0.016	8%	0.075	37%	0.112	55%	0.288	0.112	39%	0.176	61%	
20	0.516	0.262	0.021	8%	0.097	37%	0.144	55%	0.392	0.144	37%	0.248	63%	
25	0.662	0.340	0.027	8%	0.126	37%	0.187	55%	0.507	0.187	37%	0.320	63%	
30	0.755	0.419	0.034	8%	0.155	37%	0.230	55%	0.566	0.230	41%	0.336	59%	

Table 5 (cont'd): Calculations of Bioavailable Se from Figures 4-20 & 4-21 in TM6
 (Bioavailability based on mode AE's: 0.2 elemental Se; 0.45 selenite/ selenate; 0.8 Organic Se)

Bioavailable Se based on Figure 4-20 in TM6 shown as ug/L
 (Particulate Se simulated for low-flow)

Salinity	Bioavailable Se from PSP								Bioavailable Particulate Organic Se					
	Total Particulate Bioavail Se (Bio P Se)	PSP							Particulate Organic Se					
		Total	Elemental		Selenite / Selenate		Org Se		All Particulate Organic Se (Bio Org Se)	PSP Org Se		Phyto Org Se		
		Bioavail Se	Bioavail Se	% of Bio PSP	Bioavail Se	% of Bio PSP	Bioavail Se	% of Bio PSP		Bioavail Se	% of Bio Org Se	Bioavail Se	% of Bio Org Se	
ug/l	ug/l	ug/l	%	ug/l	%	ug/l	%	ug/l	ug/l	%	ug/l	%		
0	0.0053	0.002	0.00019	8%	0.00087	37%	0.00130	55%	0.00282	0.00130	46%	0.00152	54%	
2.5	0.0055	0.002	0.00018	8%	0.00085	37%	0.00127	55%	0.00295	0.00127	43%	0.00168	57%	
5	0.0050	0.002	0.00018	8%	0.00081	37%	0.00121	55%	0.00297	0.00121	41%	0.00176	59%	
10	0.0045	0.002	0.00018	8%	0.00083	37%	0.00124	55%	0.00316	0.00124	39%	0.00192	61%	
15	0.0045	0.002	0.00018	8%	0.00083	37%	0.00124	55%	0.00332	0.00124	37%	0.00208	63%	
20	0.0045	0.002	0.00018	8%	0.00083	37%	0.00124	55%	0.00340	0.00124	36%	0.00216	64%	
25	0.0045	0.002	0.00019	8%	0.00087	37%	0.00130	55%	0.00338	0.00130	38%	0.00208	62%	
30	0.0044	0.002	0.00019	8%	0.00089	37%	0.00132	55%	0.00332	0.00132	40%	0.00200	60%	

Table A.6-5 (continued)
Calculations of Bioavailability Se from Figures 4-20 and 4-21 in TM6

Table 5 (cont'd): Calculations of Bioavailable Se from Figures 4-20 & 4-21 in TM6
 (Bioavailability based on modle AE's: 0.2 elemental Se; 0.45 selenite/ selenate; 0.8 Organic Se)

Bioavailable Se based on Figure 4-21 in TM6 shown as ug/g
 (Particulate Se simulated at Carquinez Straight)

Date	Total Particulate Bioavail Se (Bio P Se)	Bioavailable Se from PSP							Bioavailable Particulate Organic Se				
		PSP							Particulate Organic Se				
		Total	Elemental		Selenite / Selenate		Org Se		All Particulate Organic Se (Bio Org Se)	PSP Org Se		Phyto Org Se	
		Bioavail Se	Bioavail Se	% of Bio PSP	Bioavail Se	% of Bio PSP	Bioavail Se	% of Bio PSP		Bioavail Se	% of Bio Org Se	Bioavail Se	% of Bio Org Se
Jun-98	0.222	0.157	0.013	8%	0.058	37%	0.086	55%	0.142	0.086	61%	0.056	39%
Nov-98	0.242	0.168	0.013	8%	0.062	37%	0.092	55%	0.156	0.092	59%	0.064	41%
Mar-99	0.159	0.131	0.011	8%	0.048	37%	0.072	55%	0.088	0.072	82%	0.016	18%
Nov-99	0.448	0.230	0.018	8%	0.085	37%	0.127	55%	0.335	0.127	38%	0.208	62%

Table 5 (cont'd): Calculations of Bioavailable Se from Figures 4-20 & 4-21 in TM6
 (Bioavailability based on modle AE's: 0.2 elemental Se; 0.45 selenite/ selenate; 0.8 Organic Se)

Bioavailable Se based on Figure 4-21 in TM6 shown as ug/L
 (Particulate Se simulated at Carquinez Straight)

Date	Total Particulate Bioavail Se (Bio P Se)	Bioavailable Se from PSP							Bioavailable Particulate Organic Se				
		PSP							Particulate Organic Se				
		Total	Elemental		Selenite / Selenate		Org Se		All Particulate Organic Se (Bio Org Se)	PSP Org Se		Phyto Org Se	
		Bioavail Se	Bioavail Se	% of Bio PSP	Bioavail Se	% of Bio PSP	Bioavail Se	% of Bio PSP		Bioavail Se	% of Bio Org Se	Bioavail Se	% of Bio Org Se
Jun-98	0.0116	0.009	0.00071	8%	0.00329	37%	0.00490	55%	0.00730	0.00490	67%	0.00240	33%
Nov-98	0.0069	0.003	0.00027	8%	0.00126	37%	0.00187	55%	0.00507	0.00187	37%	0.00320	63%
Mar-99	0.0149	0.012	0.00092	8%	0.00426	37%	0.00634	55%	0.00794	0.00634	80%	0.00160	20%
Nov-99	0.0045	0.002	0.00019	8%	0.00087	37%	0.00130	55%	0.00330	0.00130	39%	0.00200	61%

TECHNICAL MEMORANDUM 2: NORTH SAN FRANCISCO BAY SELENIUM DATA SUMMARY AND SOURCE ANALYSIS

July 2008

Prepared for:
Regional Water Quality Control Board
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ABBREVIATIONS

BASMAA	Bay Area Stormwater Management Agencies Association
cfs	cubic feet per second
mgd	million gallon per day
NDOI	Net Delta Outflow Index
NSFB	North San Francisco Bay
psu	Practical Salinity Unit
RMP	Regional Monitoring Program
SFEI	San Francisco Estuary Institute
SSC	Suspended Sediment Concentration
SWAMP	Surface Water Ambient Monitoring Program
SFBRWQCB	San Francisco Bay Regional Water Quality Control Board
TMDL	Total Maximum Daily Load
TSM	Total Suspended (Particulate) Material

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1. INTRODUCTION

North San Francisco Bay (NSFB) including Suisun Bay, Carquinez Strait, San Pablo Bay and Central Bay, shown in Figure 1-1, is listed as being impaired for selenium under section 303(d) of the Clean Water Act. This listing was based, in part, on elevated concentrations in white sturgeon and diving ducks in the 1980s and is more than a decade old. There is an ongoing effort by the San Francisco Bay Regional Water Board to prepare a TMDL for selenium in North San Francisco Bay with the most up-to-date information. This technical memorandum has been prepared in support of the TMDL development effort. The purpose of this memorandum is two-fold: provide a summary of relevant water and sediment selenium data in the North Bay and to develop a quantitative estimate of the sources of selenium to the waters of the North Bay. In addition to this document, two other technical memorandums are under preparation. The first of these assesses the scientific literature to develop recommendations for selenium toxicological endpoints in the North Bay, and the second presents a conceptual model of selenium behavior in the North Bay, with an emphasis on describing the biogeochemical processes relating selenium sources to concentrations in biological tissues. Information in these memorandums will support the development of a mechanistic model of selenium in NSFB linking sources to endpoints of interest in the TMDL.

There has been a long history of research on selenium sources, transport, and biological uptake in San Francisco Bay, the Delta, and in the Central Valley (e.g., Cutter, 1989; Cutter and San Diego-McGlone, 1990; Cutter and Cutter, 2004; Presser and Luoma, 2006; Meseck and Cutter, 2006). Starting in the mid-1980's, selenium concentrations have been monitored in the bay across the salinity gradient and in different seasons reflecting variations in freshwater flows. Major sources of selenium to the Bay-Delta identified in these previous studies include:

- San Joaquin River that receives discharge from agricultural drainage from the western San Joaquin Valley
- Selenium discharged from the effluents of North Bay refineries.
- Sacramento River, which is the dominant freshwater inflow to the Bay-Delta during the wet season.

This memorandum contains a summary of data and findings from past work, including an updated estimate of the selenium load contributions from various point and non-point sources. Over the past two decades, there have been major declines in refinery loads due to improved wastewater treatment installed in 1998; there is some evidence that San Joaquin River concentrations were lower in the late 1990s and beyond than in the 1980s, although this is not clear cut.

The data summary (Section 2) provides an overview of water and sediment data collected in and upstream of NSFB over the past two decades. Data on selenium in biota are discussed in the memo on toxicological endpoints (TM-3). The water and sediment data are presented in maps and plots to provide a visual summary and to identify major processes occurring in the North Bay. There are many ways to represent this large and complex data set. The broad objective of the data summary was to provide a reader with the spatial and temporal extent

of the data collected to date, and to evaluate whether existing data could be used to address questions of interest to the TMDL. A more detailed evaluation of the data and underlying processes will be presented in the Conceptual Model (TM-4). These data will also serve as the basis for model calibration to be performed in the next step of the TMDL development. The majority of the data collected in the bay is focused on total selenium. Speciation, particularly the concentrations of selenate, selenite, and particulate selenium, determines how efficiently selenium enters higher aquatic food web (Presser and Luoma, 2006). To the extent available, speciation data on selenium are also described.

The goal of the source analysis (Section 3) was to use data on concentrations and flow volumes of each of the identified sources in NSFB, and to take a fresh look at estimating the relative magnitudes of the key point and non-point sources of selenium. The source estimates differ from previous work in the use of more recent data and the examination of a wider range of potential sources. Sources considered include: atmospheric deposition, urban and non-urban runoff, Delta inflows and the relative contributions of the Sacramento and San Joaquin Rivers, municipal wastewater effluents, petroleum refinery effluents, and inputs from the existing reservoir of selenium in the sediments of the North Bay. Accurate quantification of sources is a key input to selenium fate and transport modeling proposed for the bay. In the event that the TMDL finds that most recent data are consistent with selenium impairment in the North Bay, the source analysis is a means to identify the loads that need to be decreased to meet targets in the bay.

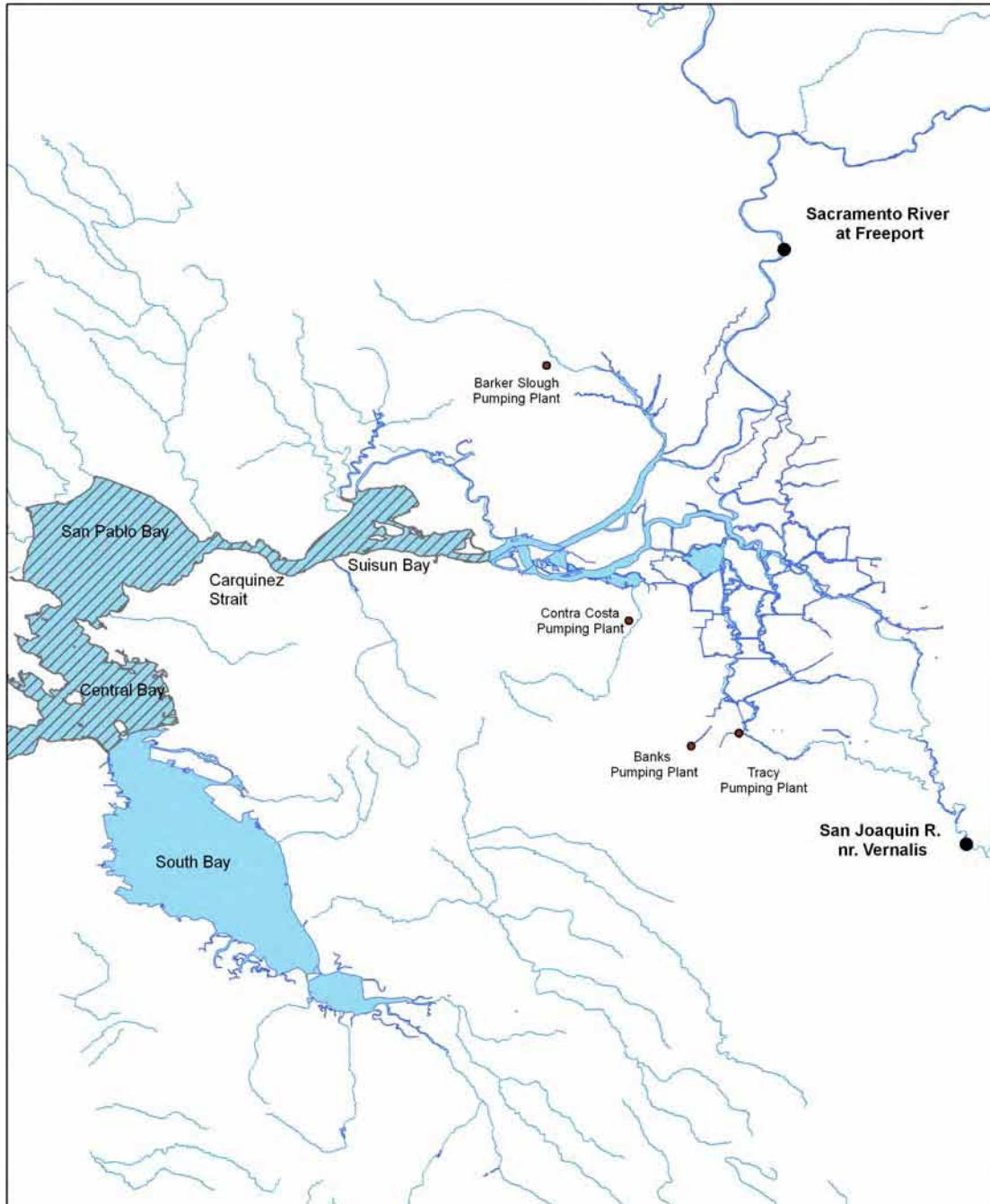


Figure 1-1 The San Francisco Bay estuary, Delta and Sacramento and San Joaquin Rivers. The cross-hatched area shows the area of interest for the North San Francisco Bay Selenium TMDL. The Sacramento River at Freeport and the San Joaquin River at Vernalis are the principal freshwater inflows into the Delta. A significant portion of the freshwater inflows are exported out of the Delta through the four pumping plants shown.

2. SELENIUM CONCENTRATIONS IN BAY WATER AND BOTTOM SEDIMENTS

2.1. GOALS OF DATA SUMMARY

A key objective of the data summary is to evaluate whether the following questions of relevance to the selenium TMDL in the NSFB can be addressed through the existing database:

- What is the distribution of selenium in the water column?
- What are the long term trends of selenium concentrations in water?
- What is the relative mix of dissolved and particulate selenium in the water column?
- How does selenium correlate with salinity and freshwater flows?
- What was the effect of refinery selenium load reduction in 1998?
- How does selenium correlate with suspended sediments and chlorophyll-a?
- What is the distribution of selenium in sediments?

In this section, the data sources used in this evaluation are first described, and plots and maps of the data are used to address each of the questions above.

2.2. DATA DESCRIPTION

Selenium concentrations in the bay water column and bottom sediments have been collected by different entities since the 1980s. The major sources of data for selenium in the North Bay are: 1) data collected by the Regional Monitoring Program (RMP) since 1993; and 2) data collected by Dr. Greg Cutter's research group at Old Dominion University¹. The RMP is a joint effort among San Francisco Estuary Institute (SFEI), the Regional Board, and local dischargers. All data collected by the Cutter research group from the mid-1980s onwards was made available to us electronically for the preparation of this and subsequent technical memorandums.

The RMP was initiated in 1993 to sample contaminant concentrations in water, sediment and bivalves. Fifteen monitoring sites were located in the North Bay (out of 26 sites in the whole bay; Figure 2-1; Table 2-1). Samples were collected at a frequency of 2-3 times a year during high flow, intermediate flow and low flow periods. Starting in 2002, EPA's Generalized Random Tessellation Stratified (GRTS) sample design approach was utilized to monitor contaminants (SEFI, 2006). Thereafter, most of the long-term sites were discontinued except for five locations noted in Table 2-1. Since 2002, each year 12 randomly selected sites in the North Bay have been sampled for selenium in the water and 24 random sites have been sampled for selenium in sediments. Water samples were collected 1-2 feet below surface. Water samples were analyzed for total and dissolved (0.45 µm filtered) concentrations, with a detection limit of 0.02 µg/L. Sediment samples were

¹ Funded by the U.S. Bureau of Reclamation, CALFED (Grant 01WRPA0077), California Department of Water Resources, and National Science Foundation, Environmental Geochemistry and Biogeochemistry Initiative (Grant: OCE-9707946).

analyzed for dry weight concentrations with detection limit of 0.01 mg/kg. Sediment samples were taken from the top 5 cm of the sediment surface.

Dr. Cutter's research group used a different sampling design to sample dissolved and particulate selenium concentrations along the estuarine transect from the Golden Gate to the Sacramento (Rio Vista) and San Joaquin River (USGS Station 757), during 1980s and again during 1997-1999 (Cutter and Cutter, 2004; Doblin et al. 2006). Samples were taken along the salinity gradient at approximately equal salinity intervals and were analyzed for dissolved selenium and selenium species (selenate, selenite, and organic dissolved selenide) at detection limits of 1.6 ng/L. Because salinity varied according to the sampling year, the spatial locations varied slightly for individual sampling events. Locations for a sampling event during November 1999 are shown in Figure 2-1 alongside RMP sampling stations. Samples were also analyzed for particulate selenium and its speciation (elemental selenium, selenite and selenate). Sampling depth is at 1-2 m below surface. The detection limit for particulate selenium was 0.4 ng/L. For the sediments, Dr. Cutter's research group sampled sediment cores at 23 locations in the Bay-Delta (Meseck, 2002). Sediment core profiles were taken from depths ranging from 5 cm to 20 cm at different locations. The cores were analyzed for total selenium, elemental selenium and selenite and selenate. Dr. Cutter's research group is the only one that has reported selenium speciation in the bay.

Table 2-1
RMP long-term sampling locations in the North Bay.

Site Code	Site Name	Sample Matrix	Period of data
BC10*	Central Bay/Yerba Buena Island	Water, sediment, bivalve	1993-2005
BC21	Central Bay/Horseshoe Bay	Sediment, bivalve	1993-2001
BC30	Central Bay/Richardson Bay	Water, sediment	1993-2001
BC41	Central Bay/Point Isabel	Water, sediment	1993-2001
BC60	Central Bay/Red Rock	Water, sediment, bivalve	1993-2001
BD15	San Pablo Bay/Petaluma River	Water, sediment, bivalve	1993-2001
BD20	San Pablo Bay	Water, sediment, bivalve	1993-2001
BD30*	San Pablo Bay/Pinole Point	Water, sediment, bivalve	1993-2005
BD40	San Pablo Bay/Davis Point	Water, sediment, bivalve	1993-2001
BD50	San Pablo Bay/Napa River	Water, sediment, bivalve	1993-2001
BF10	Suisun Bay/Pacheco Creek	Water, sediment	1993-2001
BF20*	Suisun Bay/Grizzly Bay	Water, sediment, bivalve	1993-2005
BF40	Suisun Bay/Honker Bay	Water, sediment	1993-2001
BG20*	Delta/Sacramento River	Water, sediment, bivalve	1993-2005
BG30*	Delta/San Joaquin River	Water, sediment, bivalve	1993-2005

*Sampling continued at these locations after 2002

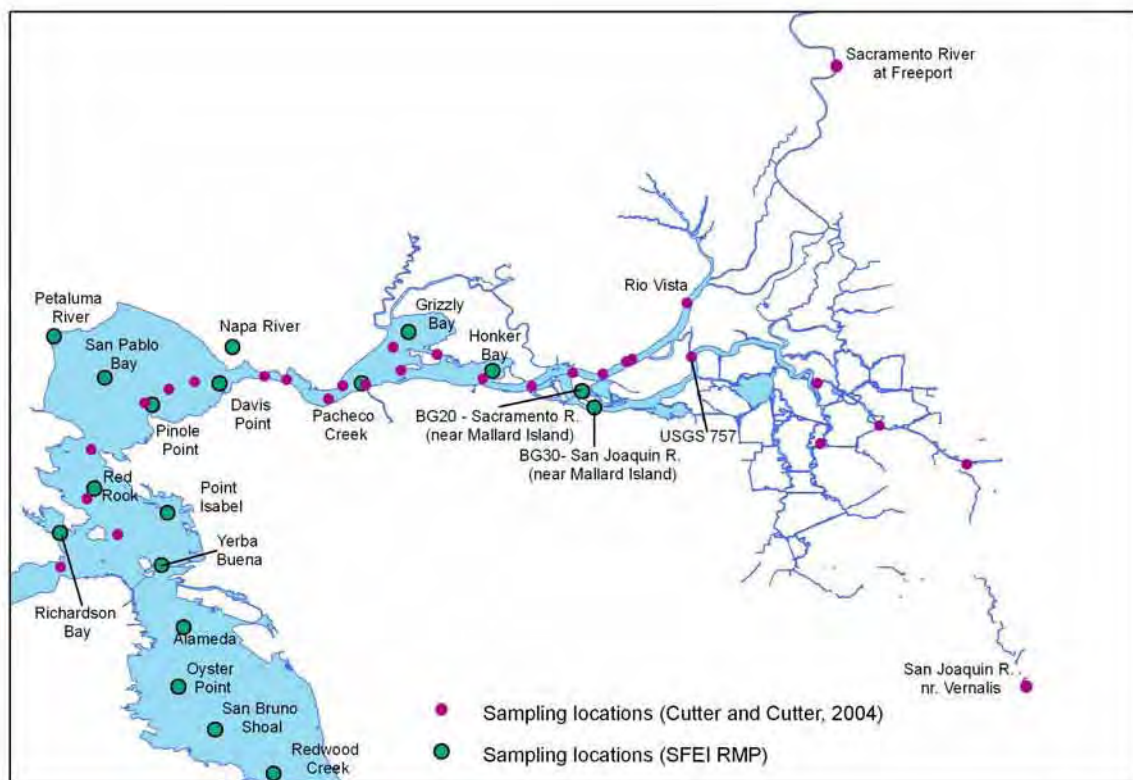


Figure 2-1 Locations of RMP long-term monitoring sites and sampling by Cutter and Cutter (2004) during November 1999.

2.3. WHAT IS THE DISTRIBUTION OF SELENIUM IN THE WATER COLUMN?

Selenium concentrations observed in the North Bay water column are generally low and mostly in the dissolved form. Over the period of 1993-2005, mean dissolved and total selenium concentrations averaged at each station were between 0.12-0.18 $\mu\text{g/L}$ and 0.13-0.24 $\mu\text{g/L}$ in the North Bay (Table 2-2 and Table 2-3). Particulate selenium (calculated as the difference between total and dissolved selenium) accounts for approximately 10% of the total. During the most recent sampling over 1999-2005, i.e., following improved wastewater control in the oil refineries in 1998 (Presser and Luoma, 2006), mean dissolved and total selenium concentrations pooled across all the long-term monitoring sites in North Bay were 0.10 $\mu\text{g/L}$ (0.03-0.24 $\mu\text{g/L}$, $n = 105$) and 0.13 $\mu\text{g/L}$ (0.04-0.45 $\mu\text{g/L}$, $n = 100$). In comparison, mean dissolved and total selenium concentrations for the period of 1993-1999 at these pooled long-term sites were 0.17 $\mu\text{g/L}$ (range: 0.03-0.44 $\mu\text{g/L}$, $n = 258$) and 0.20 $\mu\text{g/L}$ (0.02-0.5 $\mu\text{g/L}$, $n = 230$).

Spatially, total selenium concentrations are marginally higher in the mid-estuarine regions of Suisun and San Pablo Bays compared to the freshwater and marine portions (Figure 2-2). Total selenium concentrations in the Central Bay are lower, most likely due to ocean exchange and dilution. A few locations near the confluence of local tributaries (e.g., Petaluma and Napa River) show higher total selenium concentrations relative to the rest of the bay (Figure 2-2). The trends are most apparent when median values are considered.

Table 2-2
Summary of dissolved selenium concentrations in the water column for the period 1993-2005 for
the North Bay (data source: RMP).

Site Code	Site Name	Mean ($\mu\text{g/L}$)	S.D. ($\mu\text{g/L}$)	Median ($\mu\text{g/L}$)	Count
BC10	Yerba Buena Island	0.14	0.08	0.11	27
BC20	Horseshoe Bay	0.14	0.10	0.10	23
BC30	Richardson Bay	0.14	0.10	0.13	23
BC41	Point Isabel	0.14	0.09	0.10	24
BC60	Red Rock	0.15	0.10	0.12	20
BD15	Petaluma River	0.18	0.07	0.17	21
BD20	San Pablo Bay	0.15	0.06	0.14	24
BD30	Pinole Point	0.16	0.06	0.15	24
BD40	Davis Point	0.17	0.06	0.16	25
BD50	Napa River	0.16	0.06	0.16	24
BF10	Pacheco Creek	0.17	0.08	0.15	24
BF20	Grizzly Bay	0.14	0.06	0.13	25
BF40	Honker Bay	0.12	0.05	0.11	22
BG20	Sacramento River (near Mallard Island)	0.13	0.09	0.12	29
BG30	San Joaquin River(near Mallard Island)	0.16	0.09	0.14	28

S.D. - Standard deviation

Table 2-3
Summary of total selenium concentrations in the water column for the period of 1993-2005 for the North Bay (data source: RMP).

Site Code	Site Name	Mean (µg/L)	S.D. (µg/L)	Median (µg/L)	Count
BC10	Yerba Buena Island	0.16	0.09	0.12	23
BC20	Horseshoe Bay	0.17	0.12	0.11	19
BC30	Richardson Bay	0.13	0.08	0.11	22
BC41	Point Isabel	0.14	0.07	0.12	20
BC60	Red Rock	0.18	0.08	0.15	16
BD15	Petaluma River	0.24	0.09	0.25	19
BD20	San Pablo Bay	0.18	0.07	0.17	23
BD30	Pinole Point	0.18	0.08	0.17	23
BD40	Davis Point	0.21	0.08	0.18	23
BD50	Napa River	0.20	0.05	0.19	22
BF10	Pacheco Creek	0.19	0.07	0.19	22
BF20	Grizzly Bay	0.17	0.07	0.17	23
BF40	Honker Bay	0.16	0.05	0.15	22
BG20	Sacramento River (near Mallard Island)	0.15	0.08	0.13	27
BG30	San Joaquin River (near Mallard Island)	0.18	0.09	0.16	26

S.D.- Standard deviation

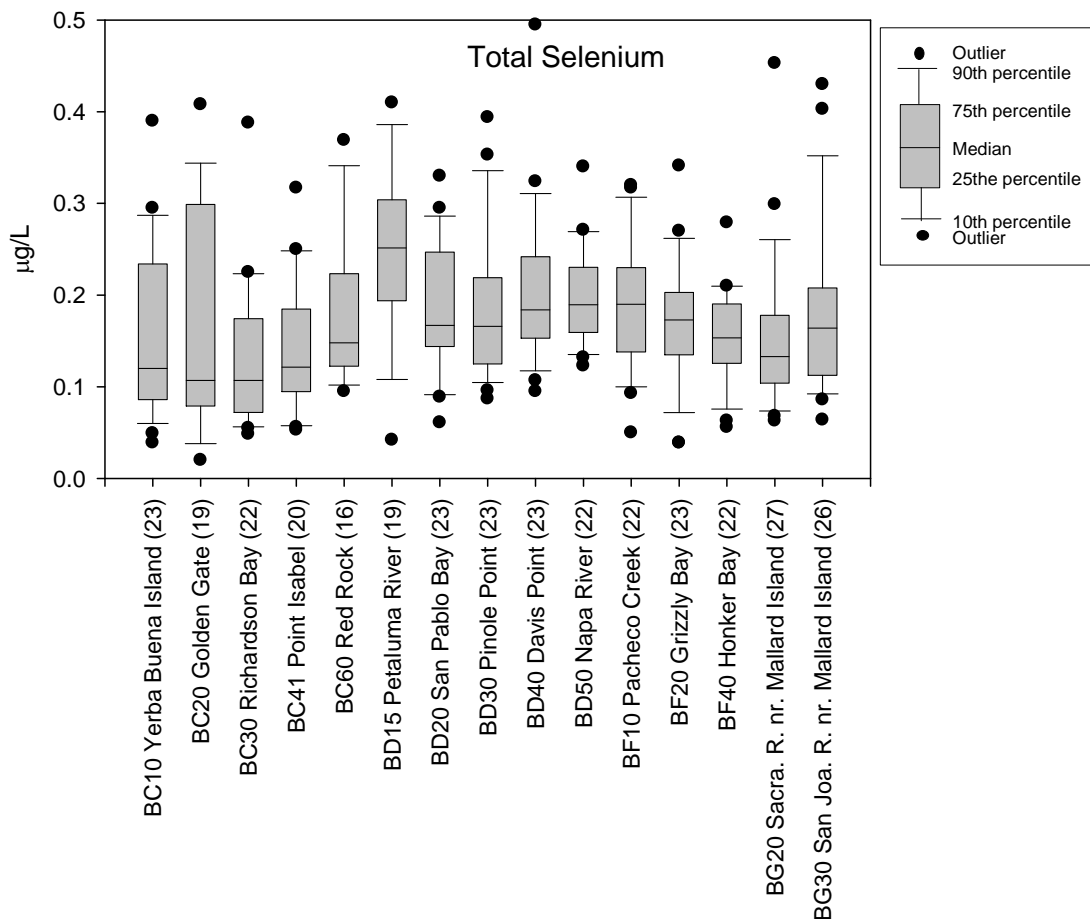


Figure 2-2 Total selenium concentrations at long-term monitoring sites for the period of 1993-2005. Values in parentheses are numbers of samples (data source: RMP).

Data from random sampling during 2002-2005 also indicated relatively low dissolved and total selenium concentrations, below 0.15 µg/L, with a whole North Bay average of 0.12 µg/L. Total selenium concentrations are higher in the upper estuary (Suisun Bay) than the San Pablo and Central Bays.

2.4. WHAT ARE THE LONG TERM TRENDS OF SELENIUM CONCENTRATIONS IN WATER?

Over the long-term, dissolved and total selenium concentrations show large temporal (both inter-annual and seasonal) variations (Figure 2-3 to Figure 2-6). For most stations in the North Bay, a weak negative correlation with time is noted, beginning in 1993. In most instances, the data show a general negative slope with time, and not an abrupt change in 1998 when refinery loads and concentrations were decreased. The temporal patterns in dissolved selenium closely resemble those in the total selenium.

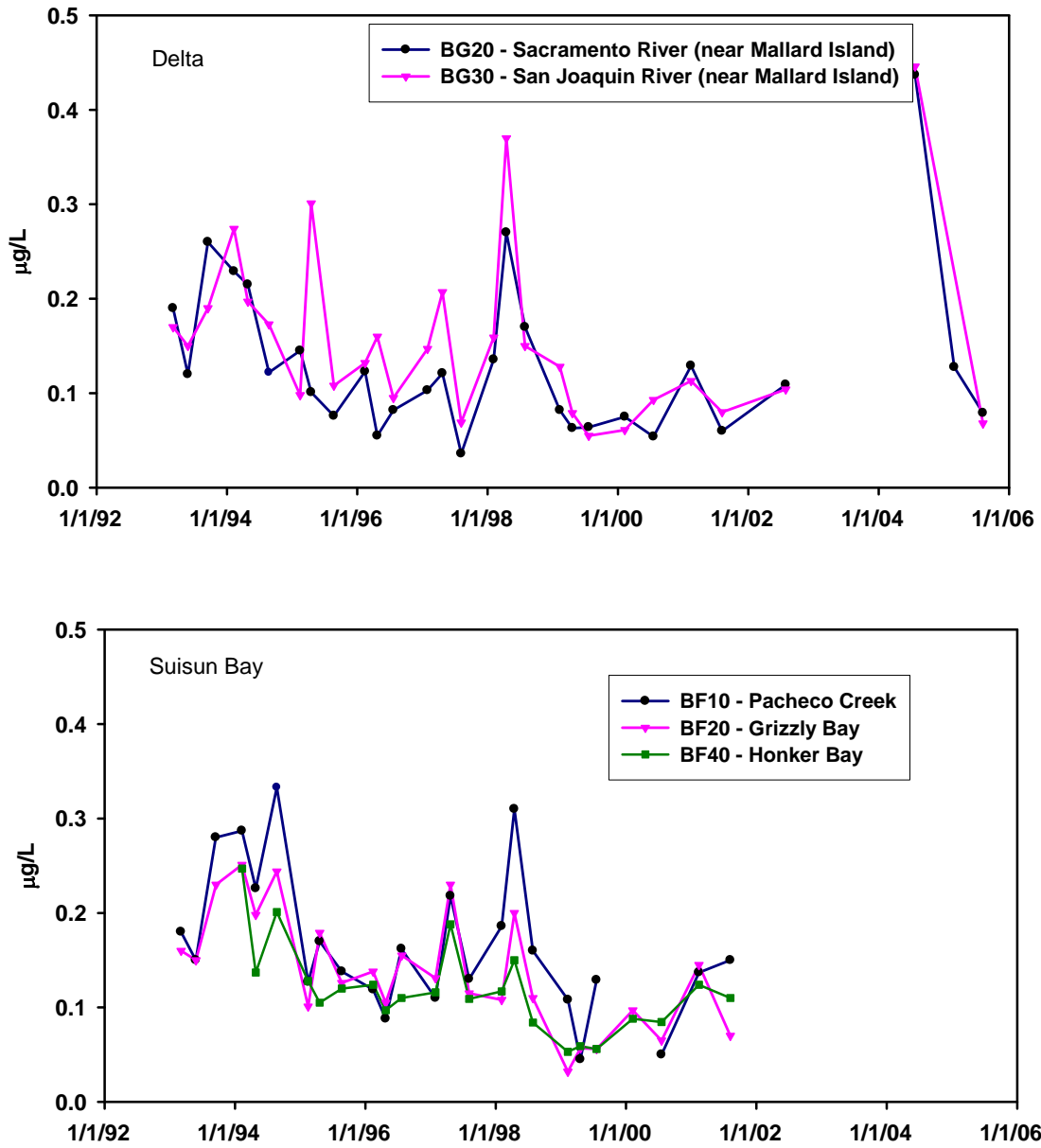


Figure 2-3 Dissolved selenium concentrations as a function of time in stations near Mallard Island and in Suisun Bay (data source: RMP).

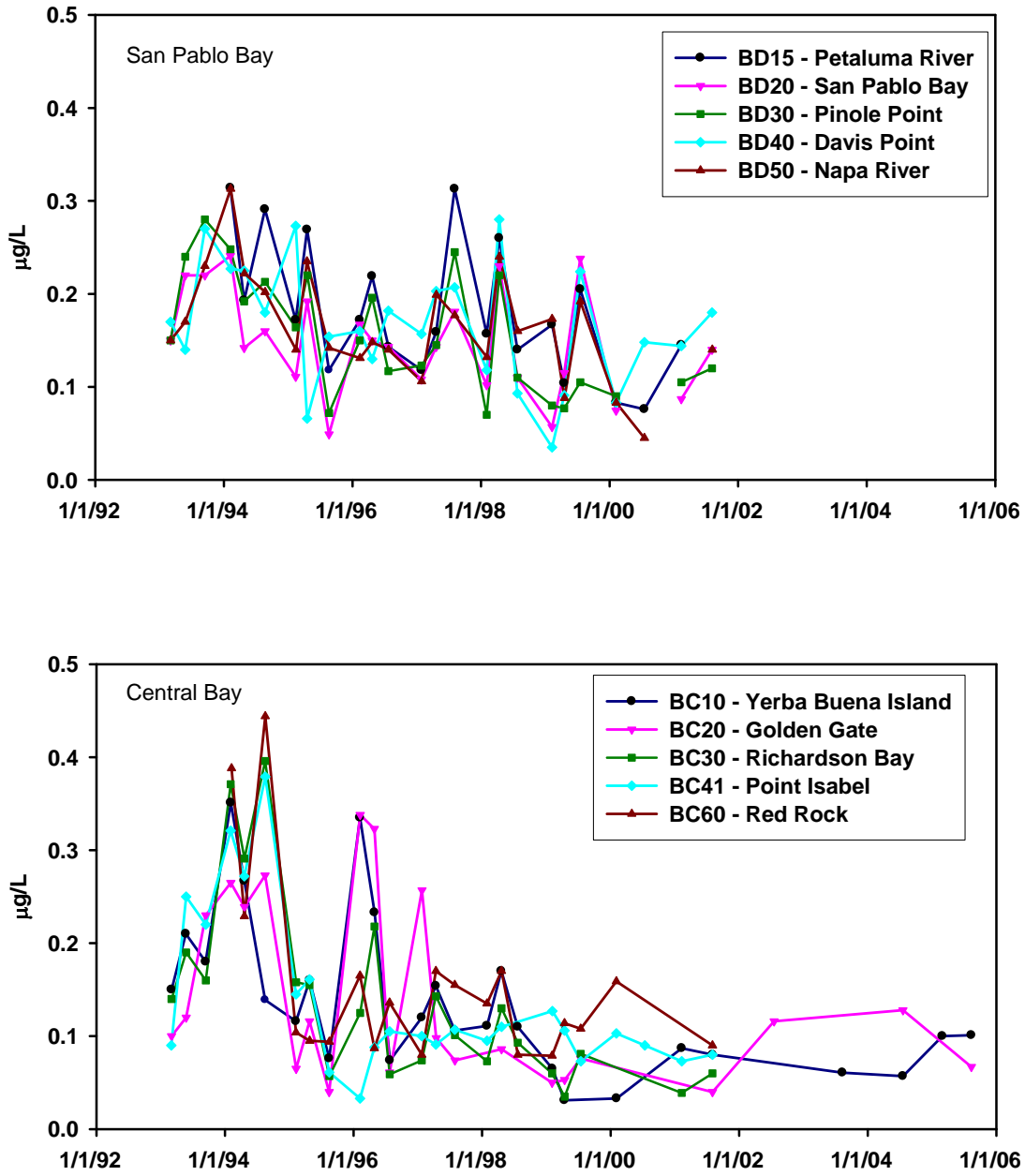


Figure 2-4 Dissolved selenium concentrations as a function of time in the San Pablo and Central Bay (data source: RMP).

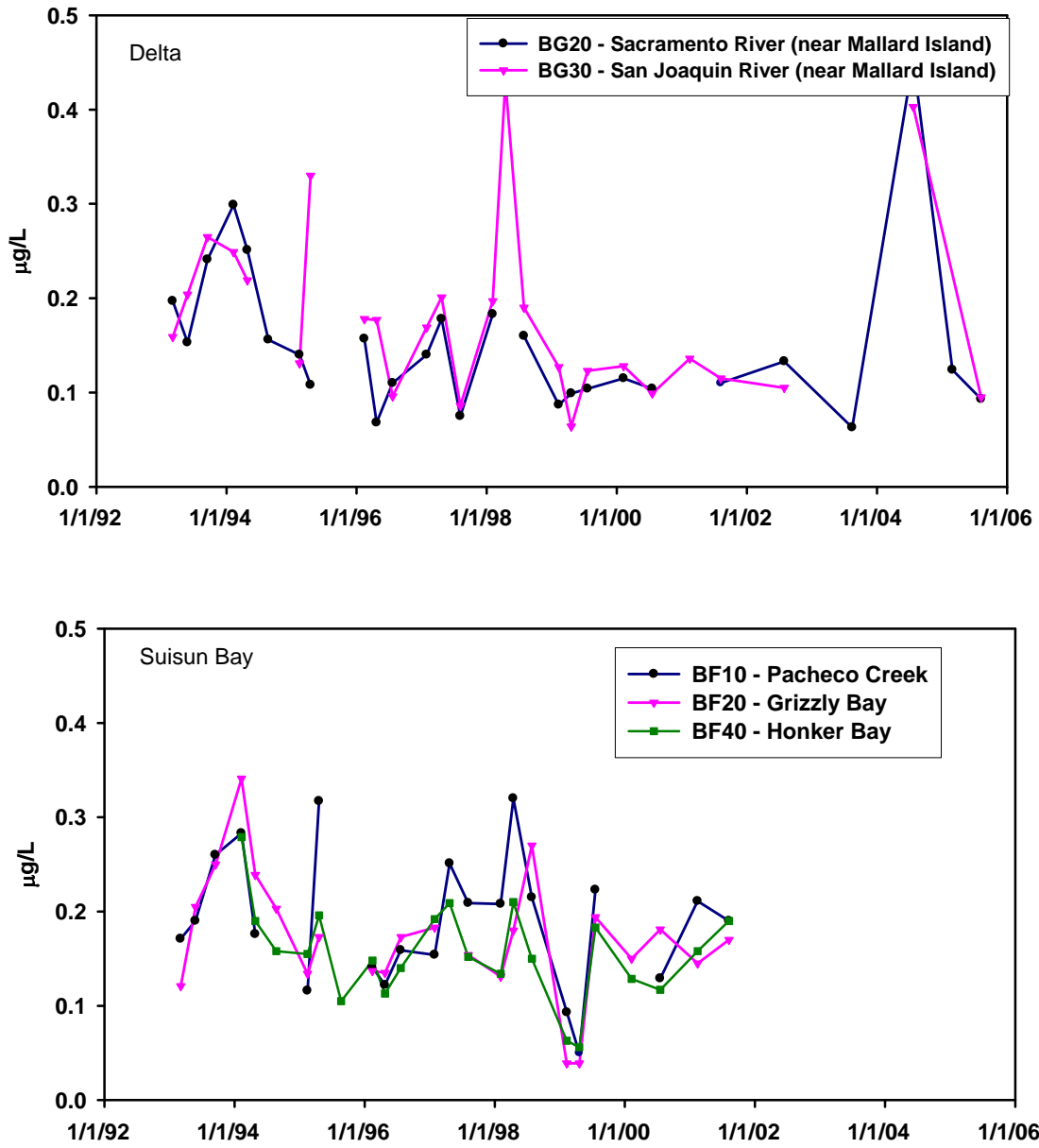


Figure 2-5 Total selenium concentrations as a function of time in stations near Mallard Island and in Suisun Bay (data source: RMP).

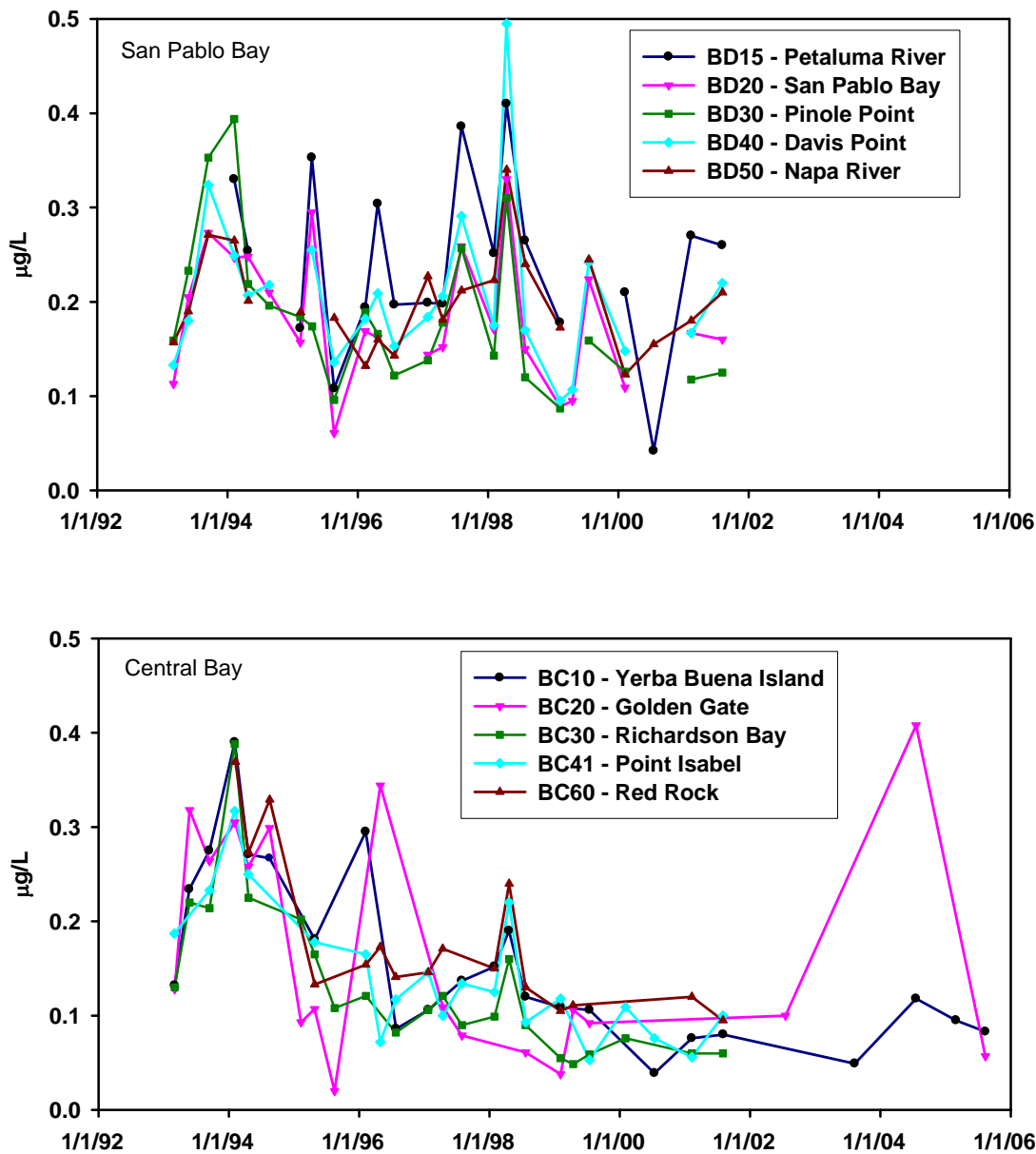


Figure 2-6 Total selenium concentrations as a function of time in the San Pablo and Central Bay (data source: RMP).

2.5. WHAT IS THE RELATIVE MIX OF DISSOLVED AND PARTICULATE SELENIUM IN THE WATER COLUMN?

Pooling all the data from the RMP monitoring indicates a close correlation between dissolved and total selenium (Figure 2-7), with the dissolved fraction representing more than two-thirds of the total selenium.

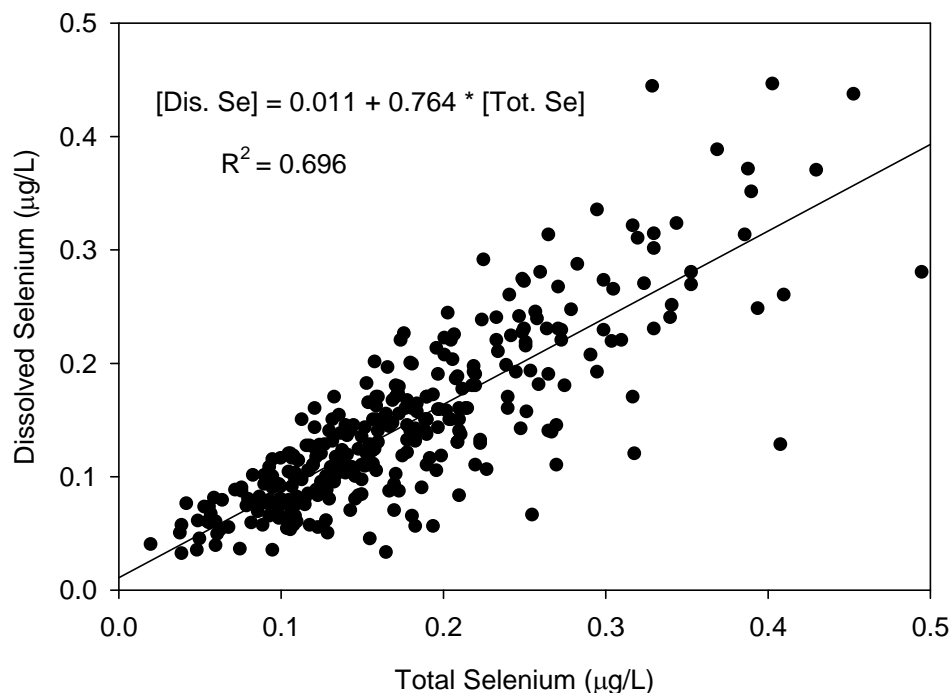


Figure 2-7 Correlation between dissolved and total selenium concentrations for long-term monitoring sites (data source: RMP).

2.6. HOW DOES SELENIUM CORRELATE WITH SALINITY AND FRESHWATER FLOWS?

Freshwater inflows from the Delta and from local tributaries, which are strongly seasonal, influence salinity and selenium concentrations in the bay. Measured dissolved selenium concentrations by RMP long-term monitoring were plotted as a function of salinity for the period before July 1998 and after July 1998, and for low flow and high flow periods (Figure 2-8 and Figure 2-9). The July 1998 cutoff represented periods before and after refinery load reductions. Transect sample data from Cutter and Cutter (2004) were also included for comparison. During low flow periods, dissolved selenium concentrations are low at salinity 0 psu, and increase in the middle of estuary (salinity 5-20 psu), and then decrease again with increase of salinity (> 25 psu). During high flow periods, selenium concentrations were generally higher at low salinity and decreased with increase of salinity or remain relatively constant (e.g. Feb 1999, Feb 2000). The observed patterns in the RMP data set agree well with the patterns observed by Cutter and Cutter (2004). Similar patterns for both low and high flow were observed for sampling dates after July 1998: during low flows, a mid-estuarine peak is more evident while concentrations were relatively constant during high flow (Figure 2-9).

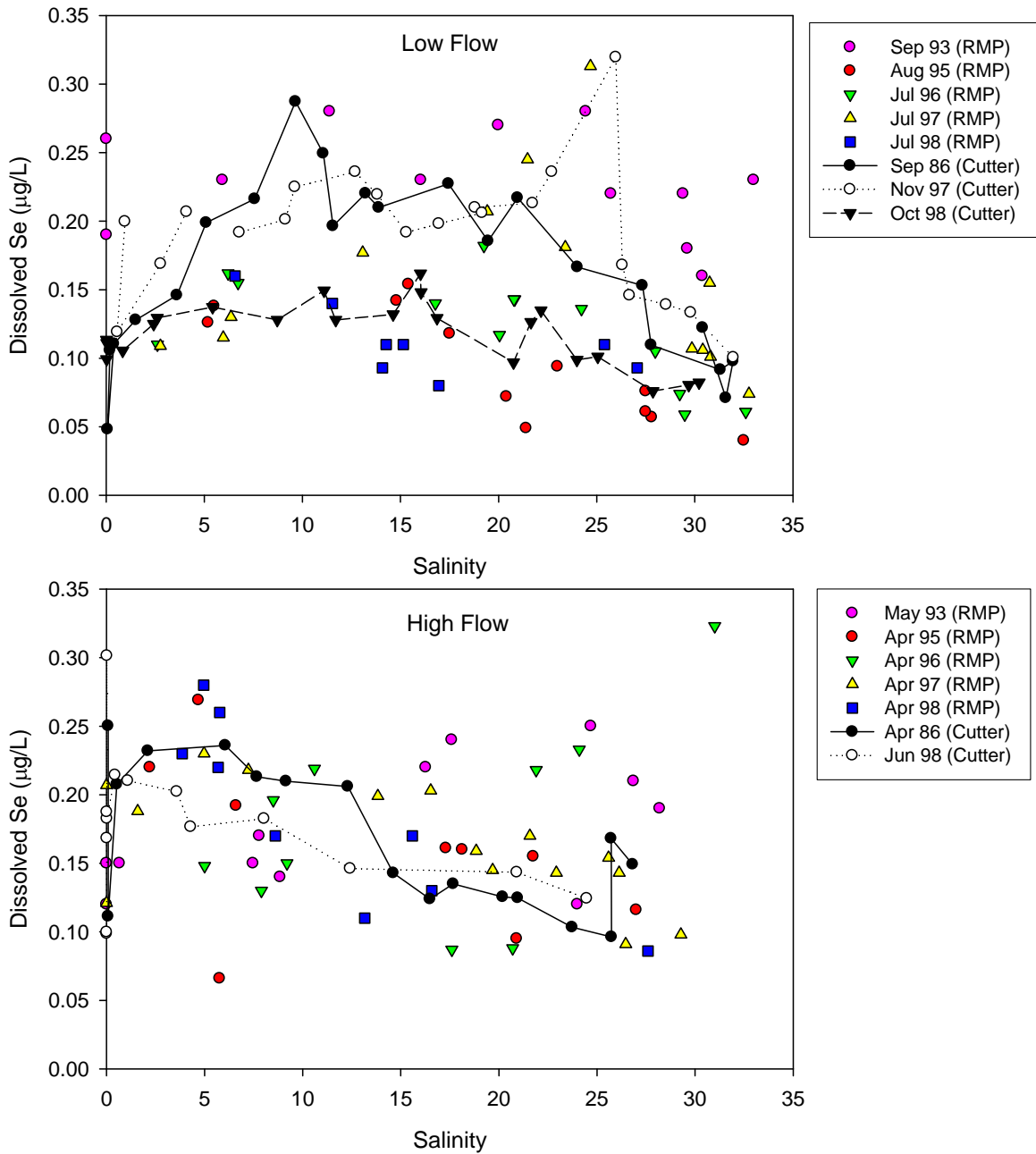


Figure 2-8 Dissolved selenium concentrations along salinity gradient during low and high flow sampling periods by RMP and Cutter and Cutter (2004) before 1999².

² Low flow and high flow for the RMP data set were defined based on sampling months: July-November (low flow), January-June (high flow). Low flow and high flow definition for the Cutter data set were the classification reported in Doblin et al. (2006): NDOI < 1.5 x 10¹⁰/d (low flow), NDOI > 8.5 x 10¹⁰/d (high flow) with October 1998 defined as low flow for simplification.

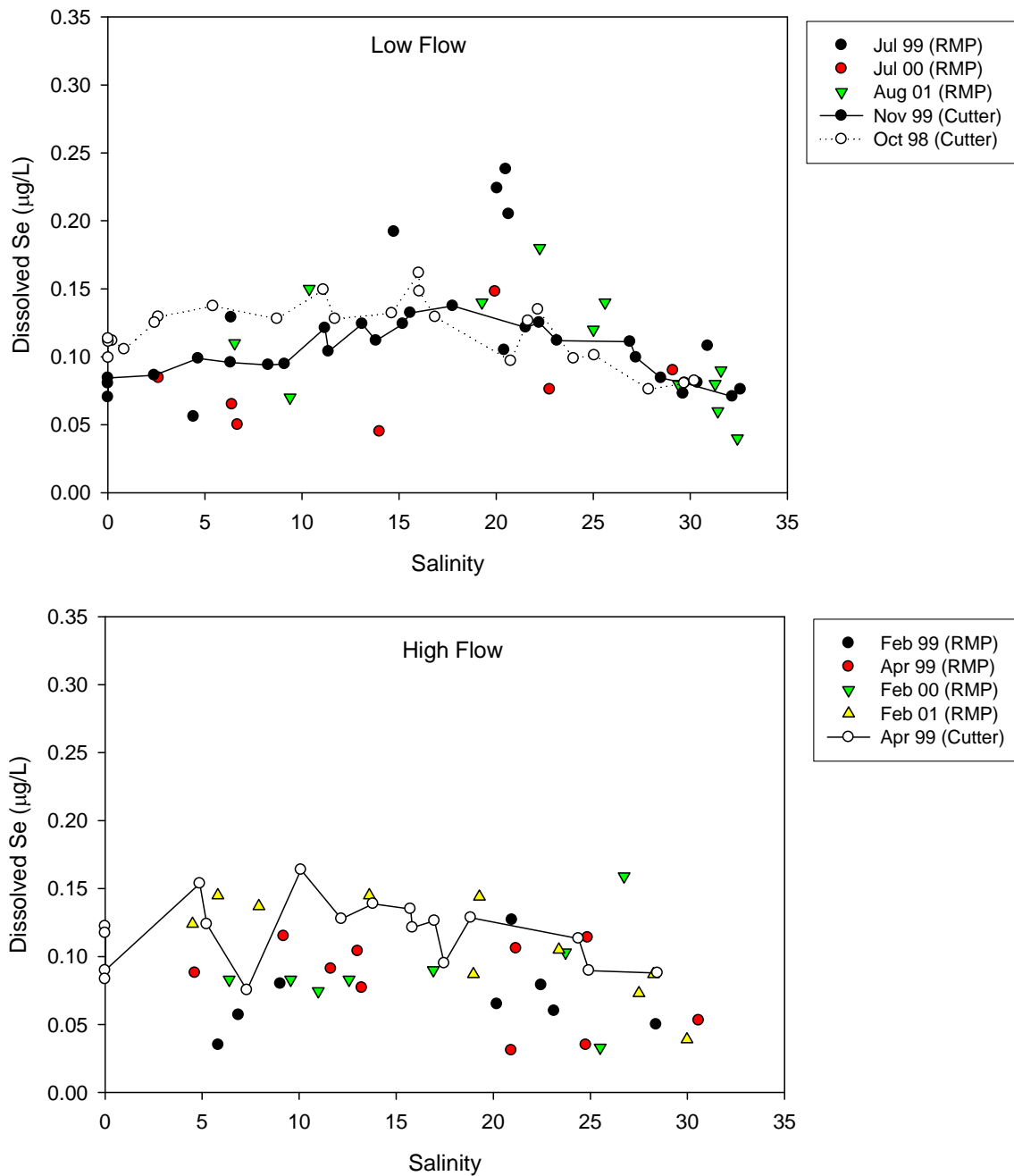


Figure 2-9 Dissolved selenium concentrations as a function of salinity during low and high flow sampling periods by RMP and Cutter and Cutter (2004) from 1999 onwards.

Selenium concentrations during the low flow period of a dry year (August 2001) indicated elevated concentrations in the Suisun Bay relative to the head of the estuary (Figure 2-10), suggesting local inputs of selenium. Maximum concentrations were observed in Suisun Bay near the Carquinez Strait. Concentrations in the San Pablo Bay remain relatively high compared to the head of estuary. Concentrations in Central Bay are lower. Salinity showed an increasing pattern from the head of estuary to the Golden Gate: from 0 to 10 psu in Suisun Bay, 25 psu in San Pablo Bay and above 30 psu in Central Bay.

During a wet period of the same year (February 2001), dissolved selenium concentrations were similar among the head of the estuary, Suisun Bay and San Pablo Bay stations (Figure 2-11). Lower concentrations were observed in the Central Bay. As expected, salinity during high flow is lower in Suisun and San Pablo Bay compared to the low flow period of the same year (August 2001).

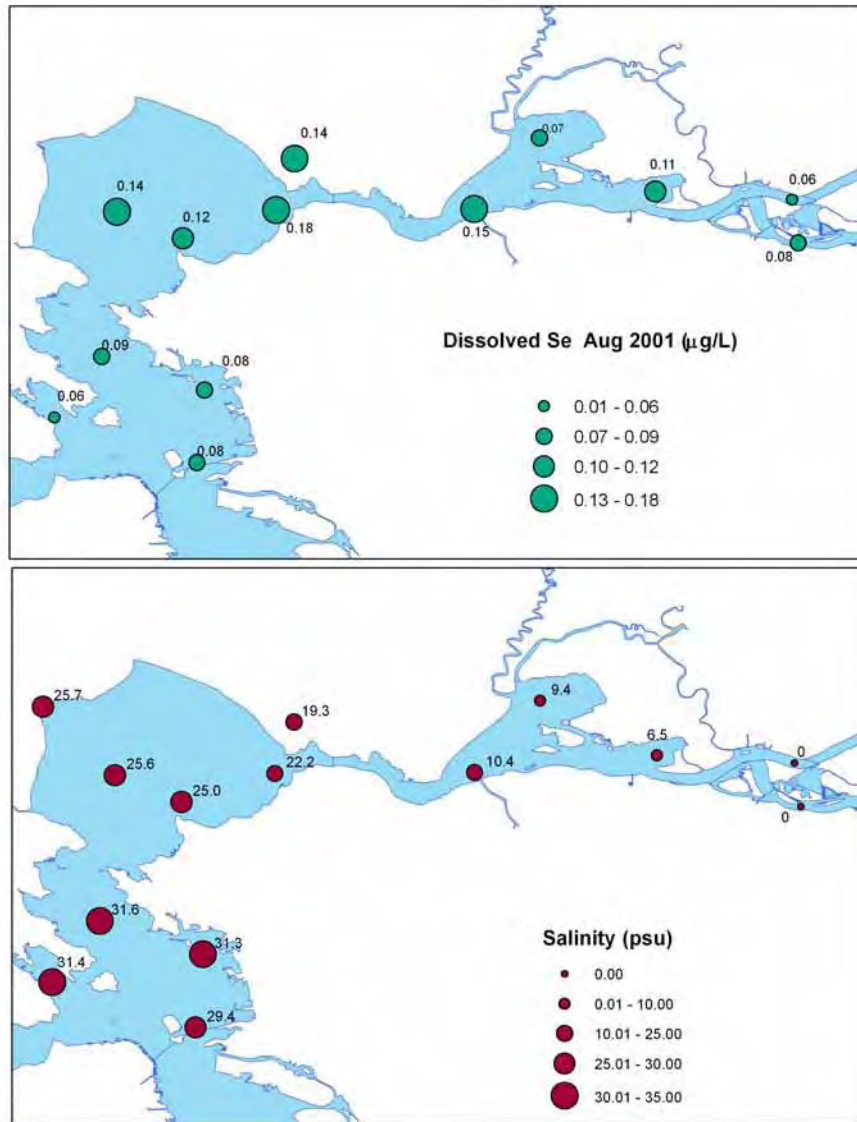


Figure 2-10 Spatial distribution of dissolved selenium and salinity during a sampling event in a dry period of a dry year (August 2001) by the RMP.

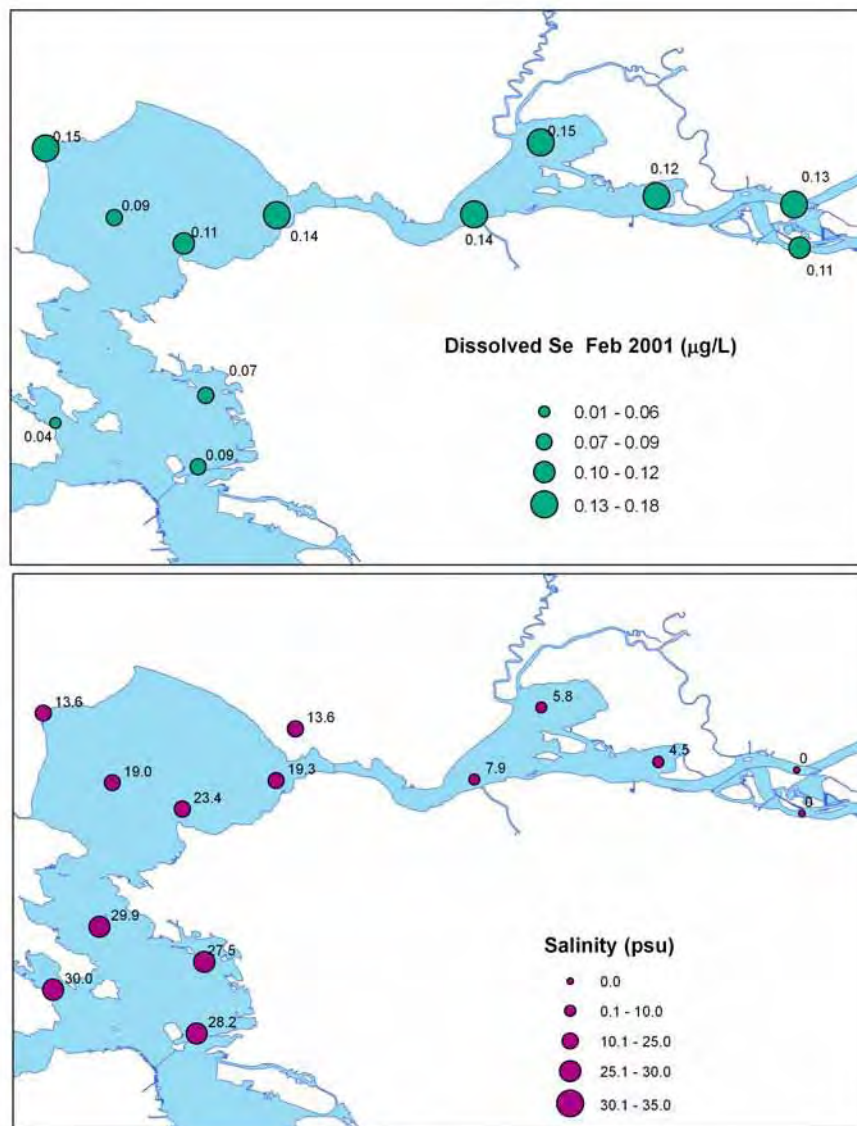


Figure 2-11 Spatial distribution of dissolved selenium and salinity during a sampling event in a wet period (February 2001) by the RMP.

During high flow periods, dissolved selenium concentrations along several salinity transects sampled by Cutter and Cutter (2004) suggested either a dilution pattern by seawater or were relatively constant throughout the bay (Figure 2-12). Dissolved selenium concentrations in April 1986 and June 1998 decreased with increase of salinity with some removal along salinity gradient, possibly due to phytoplankton uptake. Dissolved selenium concentrations were lower in April 1999 compared to April 1986 and June 1998. With the implementation of improved waste water treatment in the refineries in 1998, the most significant change in water column selenium was with respect to selenite (Cutter and Cutter, 2004). For both April 1986 and June 1998, selenite concentrations indicated an increase in the mid-estuary. In contrast, selenite concentrations for April 1999 remained low throughout the Bay (Figure 2-12). Selenate concentrations exhibited more conservative mixing behavior. Selenate concentrations in April 1999 were lower than in April 1986 and June 1998. Organic selenide

concentrations showed some variability along the salinity transect although concentrations for the three high flow periods are similar.

Dissolved selenium concentrations during low flow sampling events indicated elevated concentrations in the mid-estuary (salinity 5 -25 psu; Figure 2-13). Concentrations for October 1998 and November 1999 are generally lower than September 1986. However, total dissolved selenium concentrations are still slightly elevated in the mid-estuary. The most significant change is the observed decrease in selenite concentrations (Figure 2-13; Cutter and Cutter, 2004). Selenite concentrations for November 1999 are significantly lower than September 1986 and remain relatively constant throughout the Bay. Selenate concentrations were generally similar between the 1986 transect and October 1998 and November 1999 transects. Selenate concentrations show slightly elevated concentrations between salinity 10-20 psu. Organic selenide shows variable concentrations along the salinity transects.

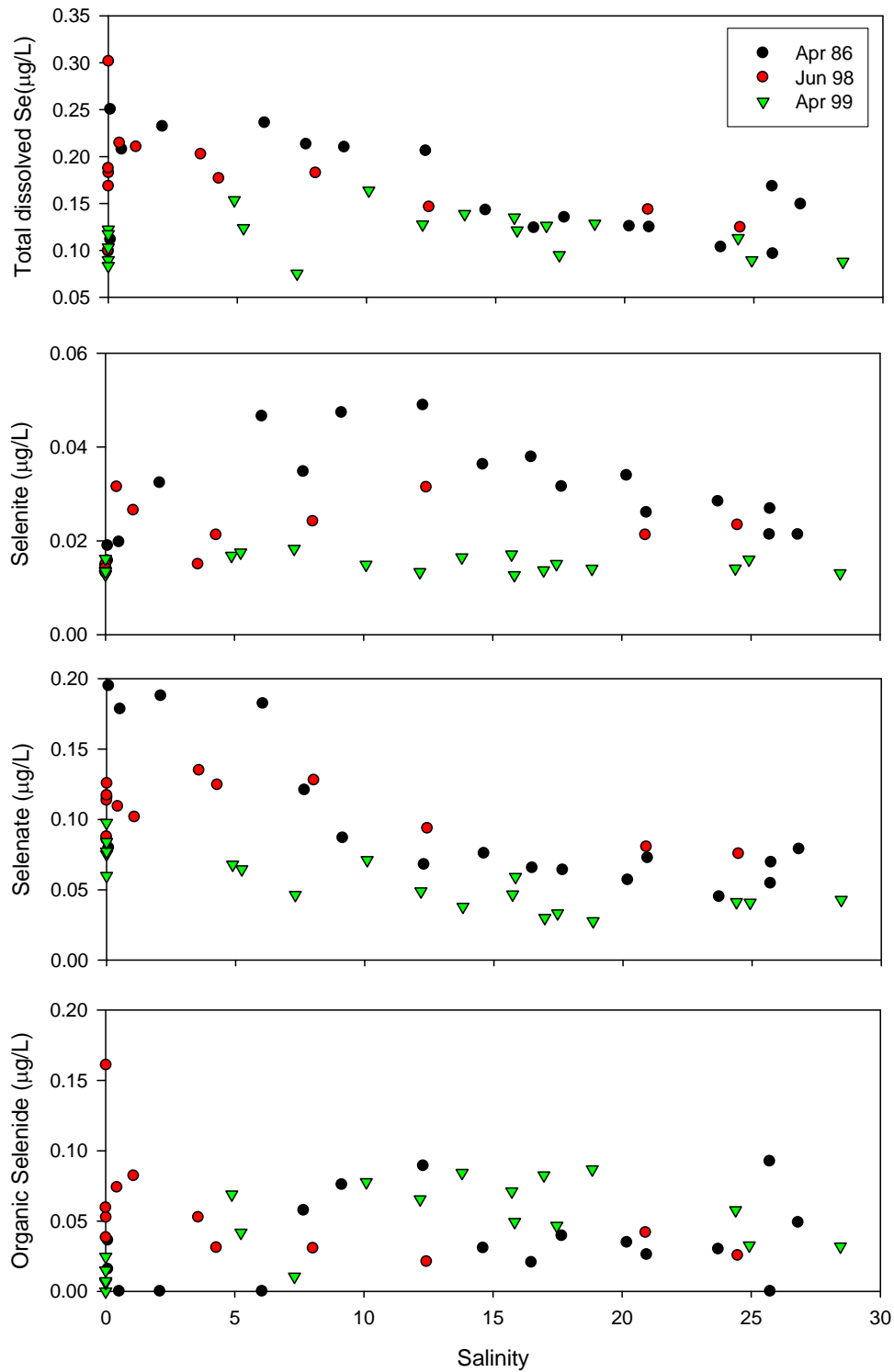


Figure 2-12 Transects of dissolved selenium, selenite, selenate, and organic selenide under high flow sampling periods (April 1986, June 1998, and April 1999; from Cutter and Cutter, 2004).

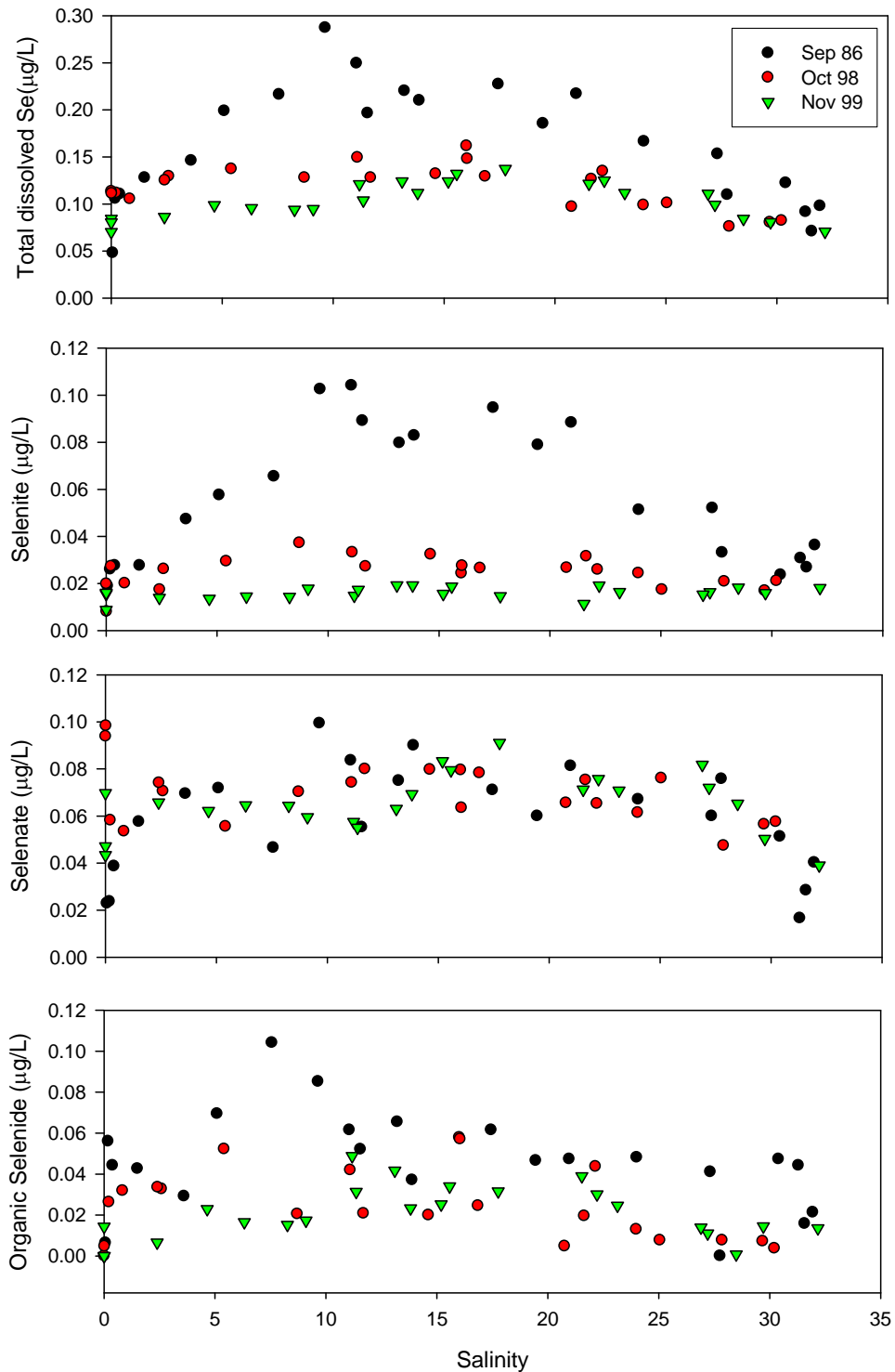


Figure 2-13 Transects of dissolved selenium, selenite, selenate and organic selenide under low flow sampling periods (September 1986, October 1998, and November 1999; from Cutter and Cutter, 2004).

2.7. WHAT WAS THE IMPACT OF REFINERY SELENIUM LOAD REDUCTIONS IN 1998?

Cutter and Cutter (2004) sampled the effluents of five refineries in the North Bay for three time periods during 1999-2000. Average dissolved selenium concentrations in the effluents of the refineries was 16.4 µg/L, a 66% decrease from average concentrations of 45.8 µg/L during 1987-1988 (Cutter and Cutter, 2004). The resulting decreases in selenium concentrations in the bay water are both evident for the low flow and high flow period (Figure 2-14).

Speciation of refinery effluent also changed dramatically after improved wastewater treatment. Average selenite concentrations at the five refineries changed from 28.2 µg/L (4.3 – 59.0 µg/L) from 1987 to 2.3 µg/L (0.3-5.0 µg/L) during the 1999-2000 (Cutter and Cutter, 2004).

Dissolved selenium speciation in the bay water column is dominated by selenate, followed by organic selenide and selenite (Table 2-4). Selenite averages 15% of total dissolved selenium in a low flow sampling event in November 1999, compared with 22% during a high flow sampling event in April 1999. Selenate was 64% and 56% of total dissolved selenium for November 1999 and April 1999, respectively. The changes in wastewater treatment at the refineries resulted in changes in speciation in the bay water column, most noticeably during low flow (Figure 2-15).

Table 2-4
Speciation of dissolved selenium in Bay water (Cutter and Cutter, 2004)

	Selenite		Selenate		Organic selenide		Total dissolved
	µg/L	% of total	µg/L	% of total	µg/L	% of total	µg/L
Apr 99 (high flow)	0.026 ± 0.006	22%	0.067 ± 0.010	56%	0.026 ± 0.017	22%	0.119 ± 0.024
Nov 99 (low flow)	0.016 ± 0.002	15%	0.067 ± 0.012	64%	0.022 ± 0.013	21%	0.105 ± 0.019
Apr 86 (high flow)	0.031 ± 0.010	19%	0.099 ± 0.094	59%	0.035 ± 0.055	21%	0.167 ± 0.062
Nov 86 (low flow)	0.057 ± 0.029	35%	0.058 ± 0.023	36%	0.047 ± 0.024	29%	0.162 ± 0.063

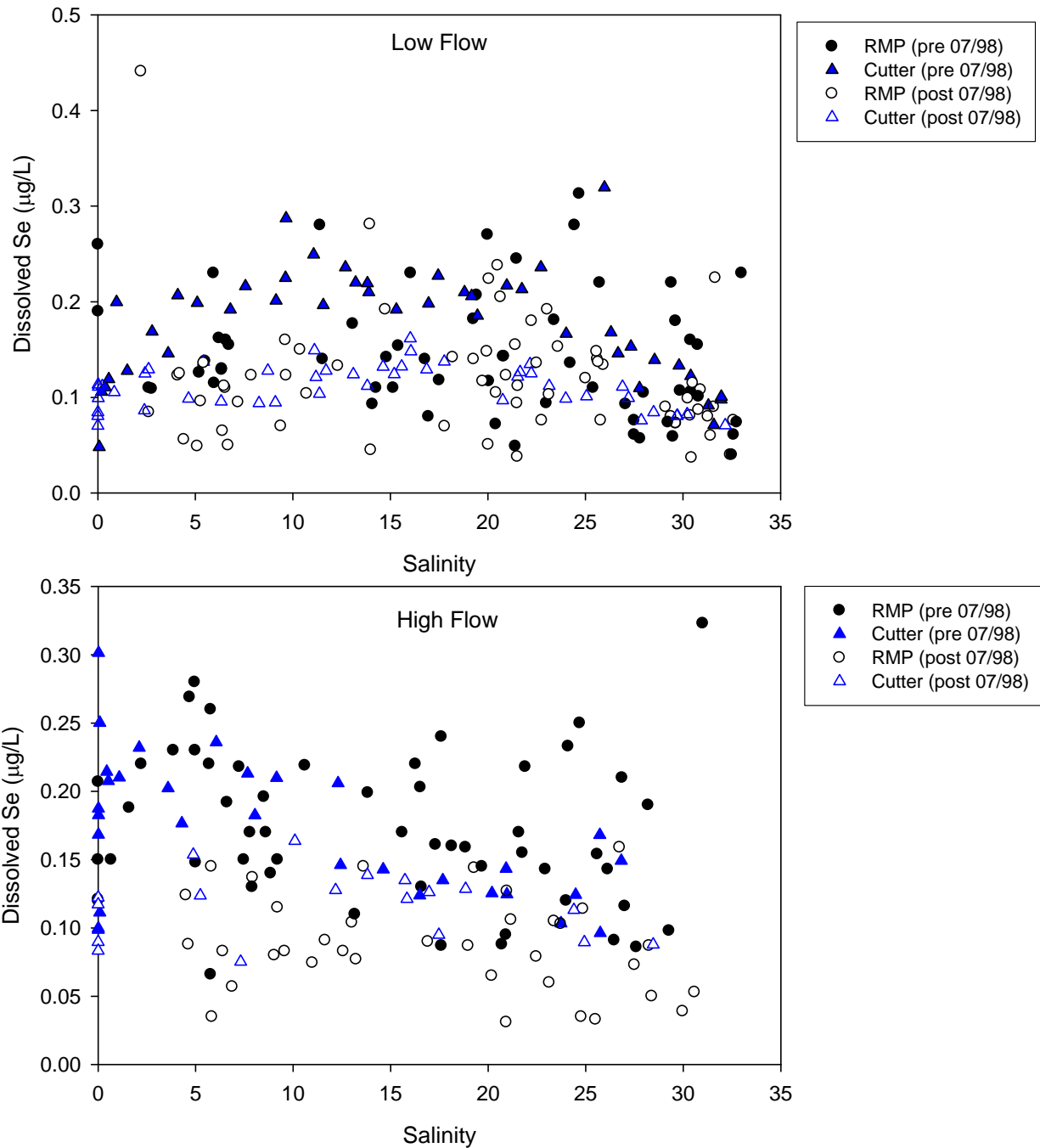


Figure 2-14 Dissolved selenium concentrations under low and high flow before and after July 1998 (data: RMP and Cutter and Cutter, 2004). The July 1998 cutoff date represents samples before and after improved wastewater treatment at the North Bay refineries.

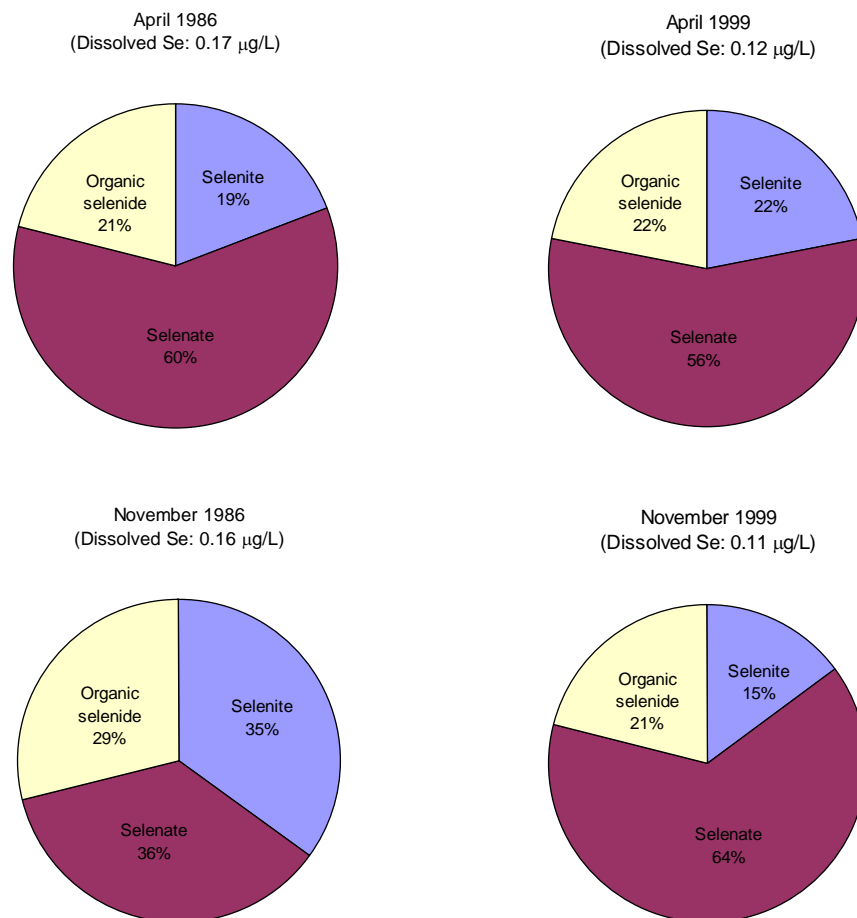


Figure 2-15 Speciation of dissolved selenium in Bay water column during different time periods (Data: Cutter and Cutter, 2004).

2.8. HOW DOES SELENIUM CORRELATE WITH SUSPENDED SEDIMENTS AND CHLOROPHYLL-A?

Doblin et al. (2006) reported the variation of total suspended particulate material (TSM),³ and selenium on particles in San Francisco Bay. Particulate selenium content, including speciation, was measured directly using material collected on 0.4 µm filters. Particulate selenium was reported as mass of selenium per unit volume of water or as mass of selenium per unit mass of particles. The latter measure normalizes for the effect of changing TSM in water samples at different locations and times.

Particulate selenium concentrations along the salinity gradient generally track the pattern in TSM, and decrease along the salinity gradient during high flow (Figure 2-16). Chlorophyll-a concentrations show some occasional elevated values for the April 1986 transect. Selenium concentrations in particulate material are generally lower during high flow than low flow (Doblin et al., 2006), however, values as high as 1.6 µg/g were measured in the bay.

³ TSM: total suspended particulate material, was determined by directly filtering 2l of water (out of 5l of sample water collected) through 142mm diameter, 0.4 µm polycarbonate membranes that were pre-weighted. The filters were dried at 40 °C and weighed for TSM concentration (Doblin et al. 2006).

During low flow, TSM concentrations also decrease slightly with an increase in salinity (Figure 2-17). TSM concentrations show occasional increases in the middle of estuary, possibly due to resuspension. Particulate selenium concentrations track the patterns in TSM (Doblin et al. 2006), most evidently for the September 1986 and November 1999 transects. Selenium concentrations in particulate material exceed values measured during high flow and also show some increase with increase of salinity (up to 2.2 $\mu\text{g/g}$). For the October 1998 and November 1999 transects, chlorophyll-*a* concentrations are relatively constant throughout the bay with some increases in the Central Bay.

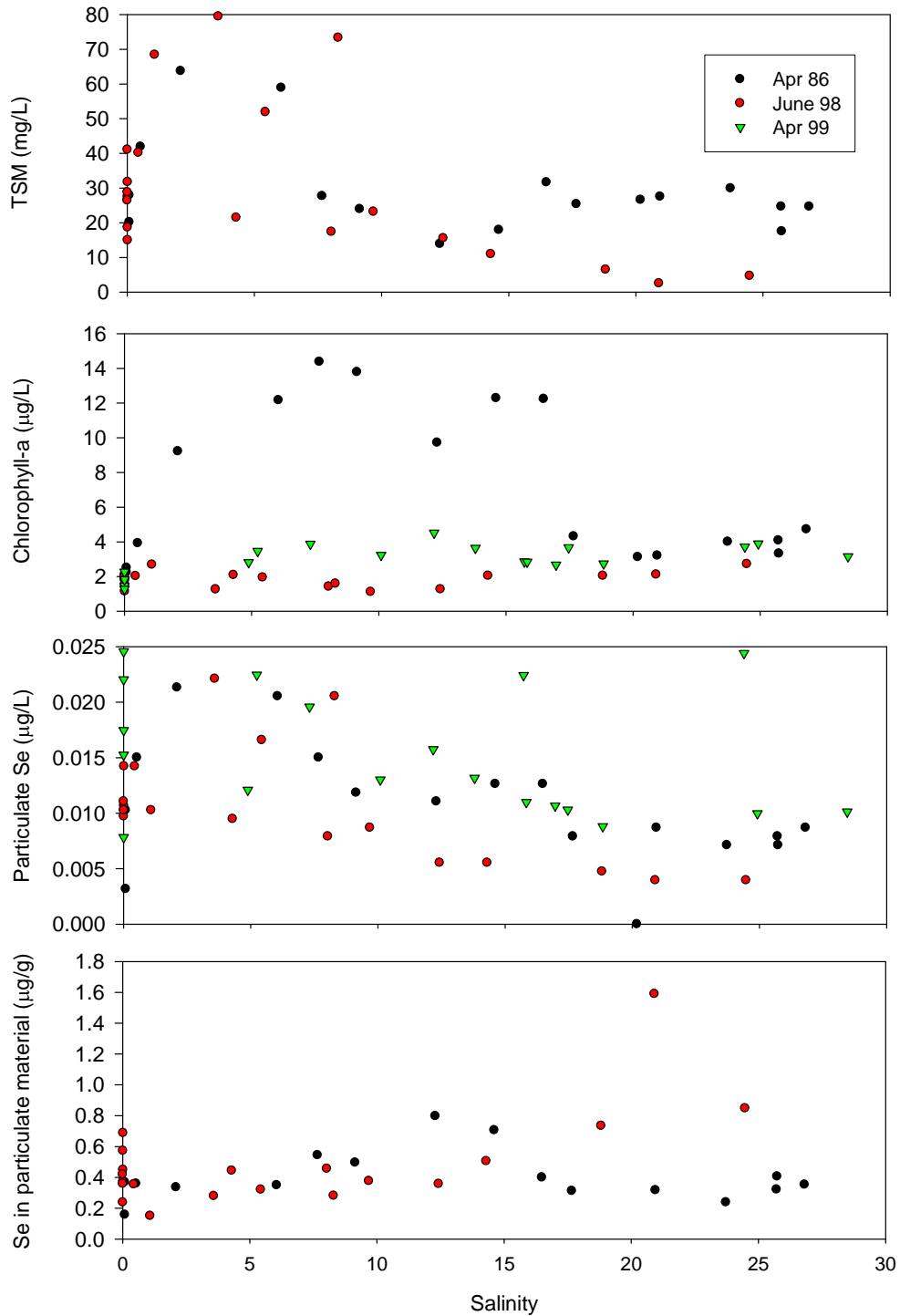


Figure 2-16 Transects of TSM, chlorophyll-a, particulate selenium and selenium in particulate material under high flow (April 1986, June 1998 and April 1999; Doblin et al. 2006).

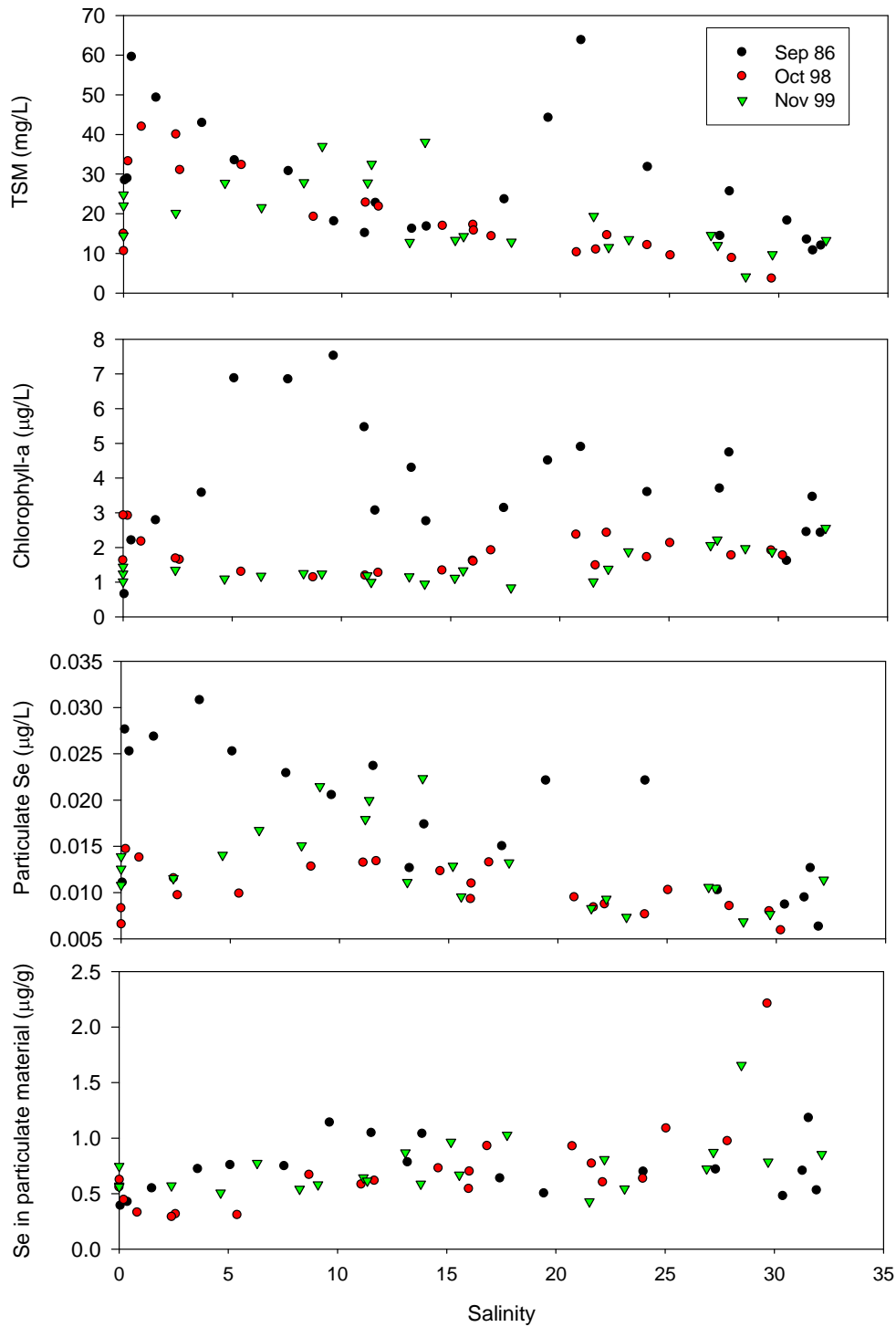


Figure 2-17 Transects of TSM, chlorophyll-a, particulate selenium and selenium in particulate material under low flow (September 1986, October 1998, and November 1999; Doblin et al. 2006).

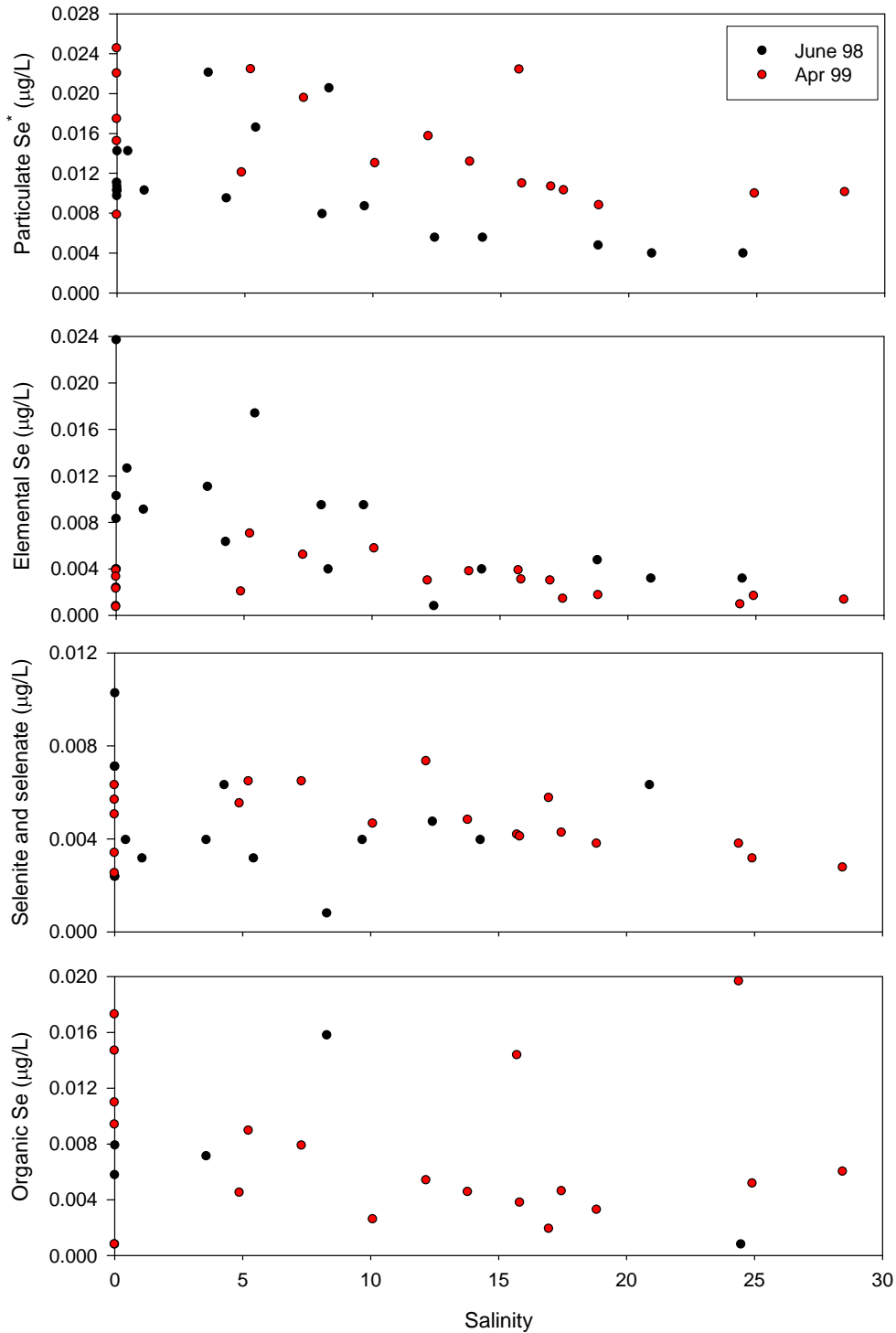
Particulate selenium concentrations, expressed as $\mu\text{g/l}$, vary less over time than TSM (Table 2-5), although selenium content in suspended particles differs between low flow and high

flow conditions. Low flow periods were found to have higher selenium content in suspended particles, most likely due to longer residence time and accumulation by phytoplankton and bacteria (Doblin et al. 2006). Selenium :Carbon ratios are higher during low flow. Selenium species on particulate material are dominated by organic selenide ($45 \pm 27\%$), followed by elemental selenium ($35 \pm 28\%$), and adsorbed selenite and selenate ($20 \pm 10\%$). The percentage of organic selenide is roughly similar during low and high flow periods. Speciation of particulate selenium along the five sampling transects are shown in Figure 2-18 and Figure 2-19.

Table 2-5
Summary of particulate concentrations during low and high flow periods (Doblin et al. 2006).

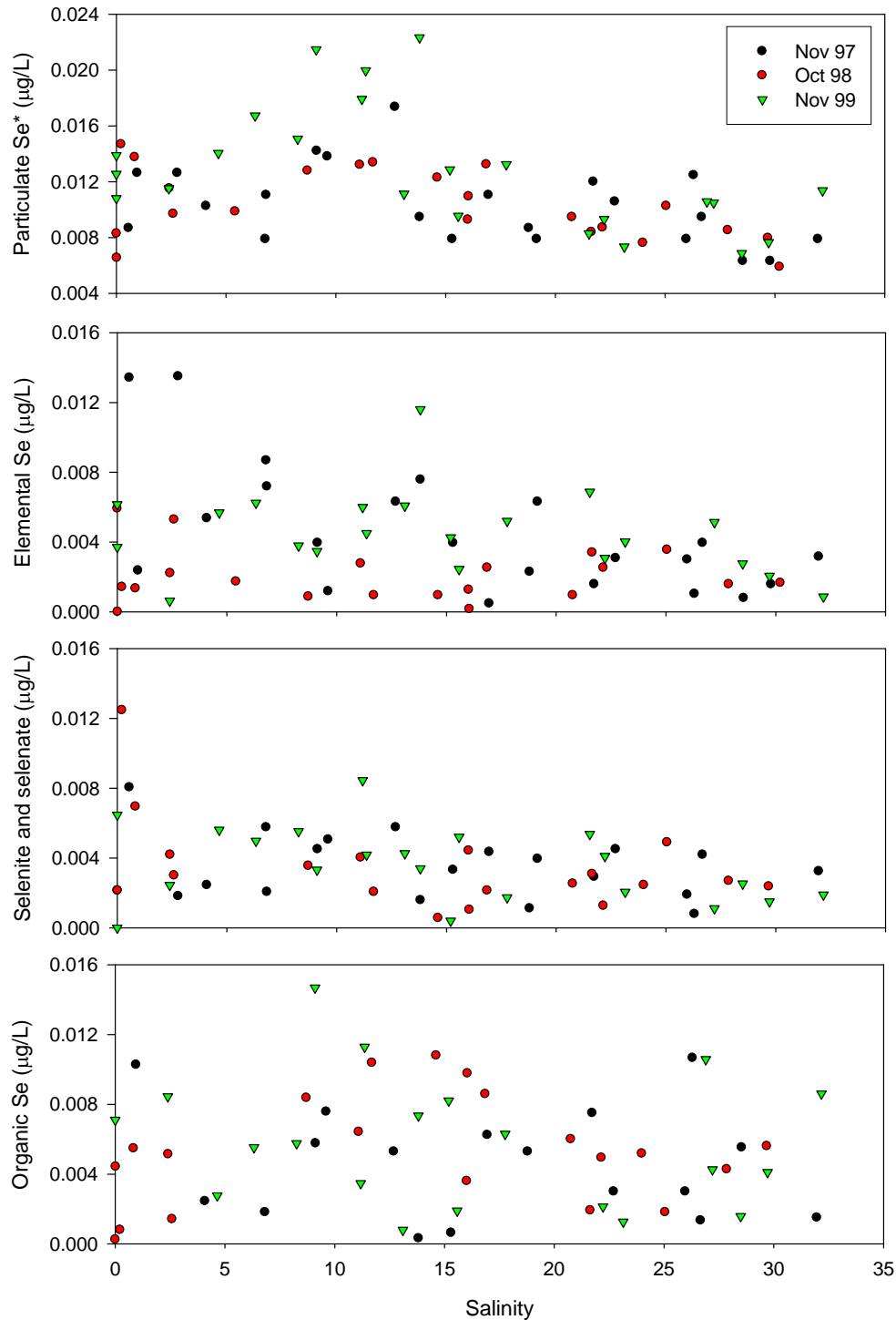
	Low Flow			High flow	
	Oct. 1998	Nov. 1999	Nov. 1997	June 1998	April 1999
TSM (mg/L)	19.1 ± 10.4	19.4 ± 8.8	13.1 ± 5.8	30.2 ± 22.0	31.2 ± 20.0
Particulate Se ($\mu\text{g/L}$)	0.010 ± 0.002	0.013 ± 0.004	0.010 ± 0.003	0.010 ± 0.005	0.015 ± 0.006
Se content in particulate ($\mu\text{g/g}$)	0.70 ± 0.41	0.73 ± 0.25	0.87 ± 0.30	0.49 ± 0.31	--
Se: C ratio ($\times 10^{-6}$)	4.7 ± 3.1	5.9 ± 2.7	6.5 ± 2.5	4.1 ± 2.0	3.0 ± 1.0

Particulate selenium concentrations are correlated with TSM (Figure 2-20). Particulate concentrations along the salinity gradient follow the pattern of TSM, which exhibit a linear decline along the salinity gradient due to mixing (Figure 2-21).



*include all adsorbed selenite and selenate, elemental and organic selenium

Figure 2-18 Transects of total particulate selenium, particulate elemental selenium, particulate adsorbed selenite and selenate, and particulate organic selenium during high flow (June 1998 and April 1999; Doblin et al. 2006).



*include all adsorbed selenite and selenate, elemental and organic selenium

Figure 2-19 Transects of total particulate selenium, particulate elemental selenium, particulate adsorbed selenite and selenate, and particulate organic selenium during low flow (November 1997, October 1998 and November 1999; Doblin et al. 2006).

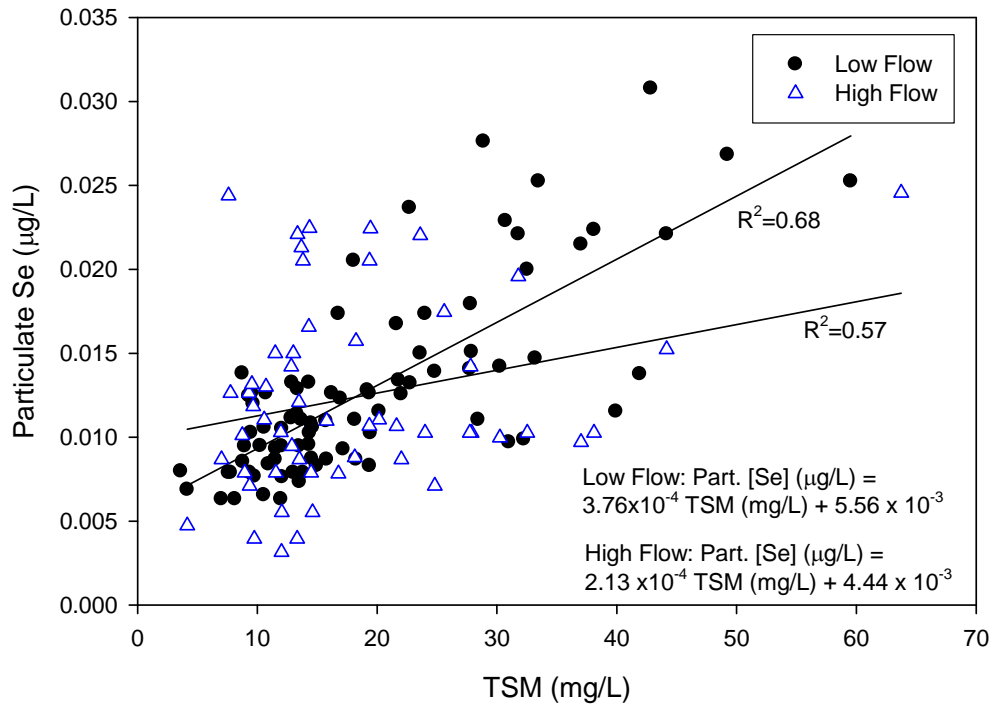


Figure 2-20 Correlation between particulate selenium and TSM under low and high flow (Data Source: G. Cutter, personal communication)

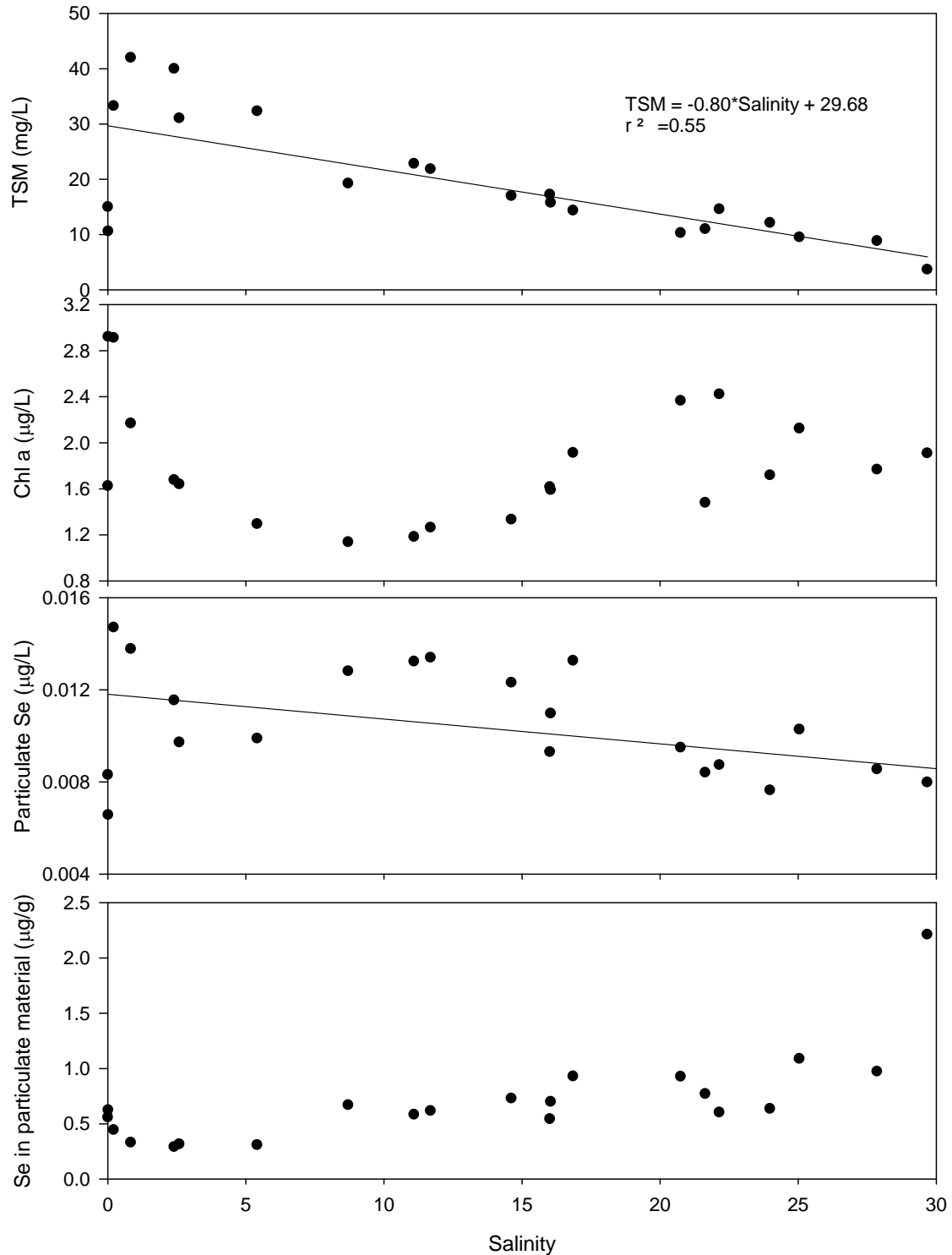


Figure 2-21 Concentrations of TSM, Chl a, and particulate selenium and selenium content in particulates for a low flow sampling event of Oct. 1998 (Doblin et al. 2006).

2.9. WHAT IS THE DISTRIBUTION OF SELENIUM IN SEDIMENTS?

Average selenium concentrations in bottom sediments of the North Bay show spatial variations at the RMP long-term monitoring sites although the total range of concentrations is not large (Figure 2-22). Sediment selenium concentrations are somewhat lower for the San Joaquin and Sacramento River stations near Mallard Island and the Central Bay stations (below 0.3 µg/g), whereas bottom sediments at sites in Grizzly Bay, San Pablo Bay and Napa River exhibit slightly elevated selenium concentrations (> 0.4 µg/g).

Sediment concentrations from RMP random sampling indicate somewhat larger spatial variation than the long-term sites because these are single point concentrations and not averages. The majority of the sediment samples have concentrations between 0.2 – 0.3 µg/g, while concentrations as high as 1.7 µg/g were also observed (Figure 2-23). The average for the whole North Bay is 0.25 µg/g. Generally, the sediment selenium concentrations observed are well below the ecological guideline of 1.5 µg/g established by SFBWQCB (1992). Selenium concentrations in seston however can reach 1.5 µg/g occasionally, as observed by Doblin et al. (2006).

Selenium concentrations in the bottom sediments are correlated to sediment grain size and organic carbon content. Sediment selenium concentrations were found to be highly related to percent fines < 0.00625 mm and percent total organic carbon (TOC) ($R^2 = 0.78$ and $R^2 = 0.56$; Figure 2-24; pooling all the data from long-term sites). Relationships between sediment selenium and percent fines and TOC are weaker for the random monitoring sites (Figure 2-25), however clear positive relationships are still observed. As illustrated in Figure 2-24, sites with low sediment selenium concentrations correspond to low percent fines in the sediments and vice versa. Meseck (2002) observed a similar strong relationship between sediment selenium and organic carbon concentrations ($R^2 = 0.85$).

Average selenium concentrations for sediment cores, 5-15 cm deep, collected by G. Cutter's research group range between 0.22-0.41 µg/g in the North Bay. Selenium in sediment cores is found to be dominated by elemental selenium (Meseck, 2002). Elemental selenium accounts for a median of 45% of the total selenium in the sediments across the sites, with selenite and selenate accounting for a median of 17%. The difference between total, elemental and selenite and selenate is the organic selenium. Selenium concentrations are generally uniform in the sediment cores, although some variations along the depth were observed (Cutter, unpublished data).

Long term data from the RMP indicated that despite sediment selenium concentrations showing inter-annual or seasonal variations, concentrations are generally stable at the monitoring sites except in early 1990s (Figure 2-26 and Figure 2-27).

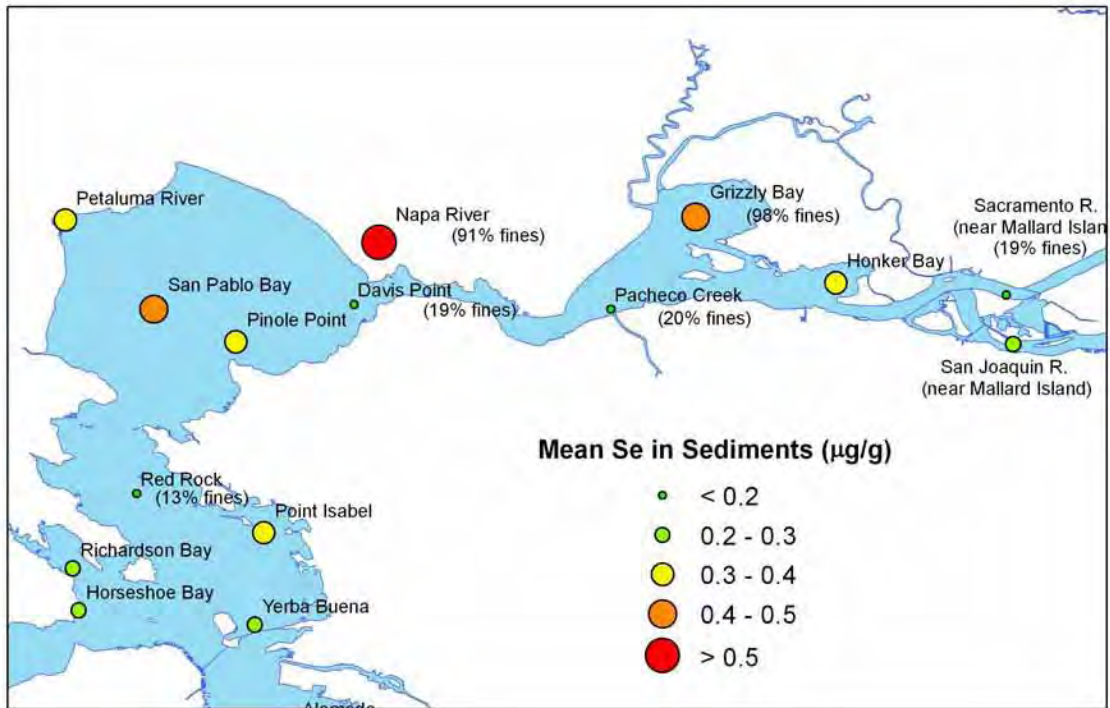


Figure 2-22 Mean selenium concentrations in sediments for the period of 1993-2005 (data source: RMP).

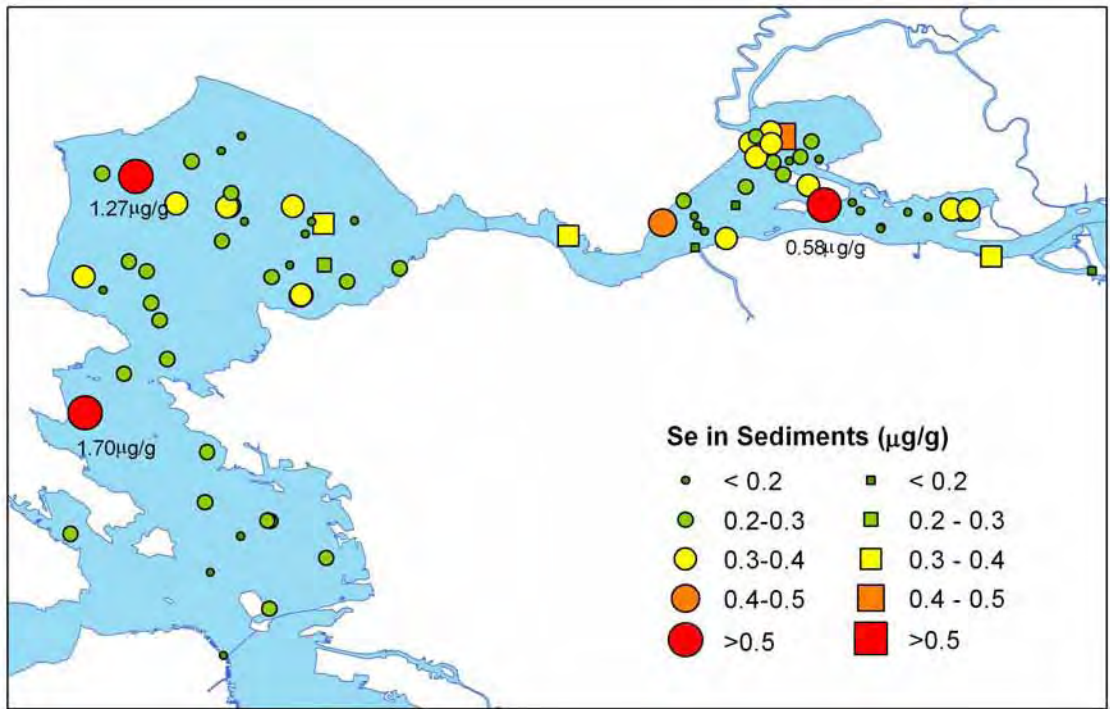


Figure 2-23 Selenium concentrations in sediments with data from RMP random sampling sites (circles) and data collected by G. Cutter's research group (squares). Numbers shown are individual values from the sampling.

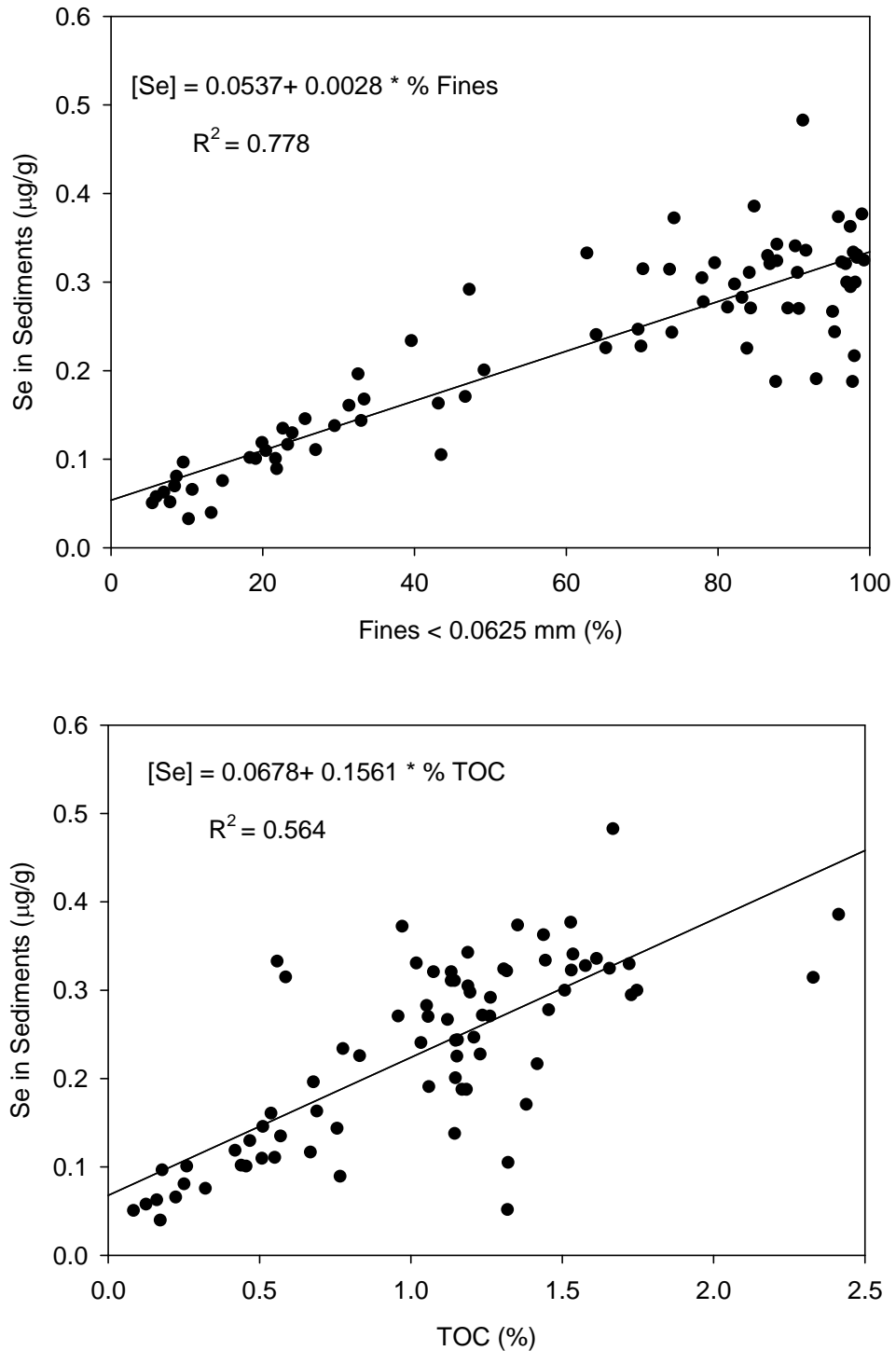


Figure 2-24 Relationship between selenium concentrations in sediments and sediment characteristics at long-term sites (data source: RMP).

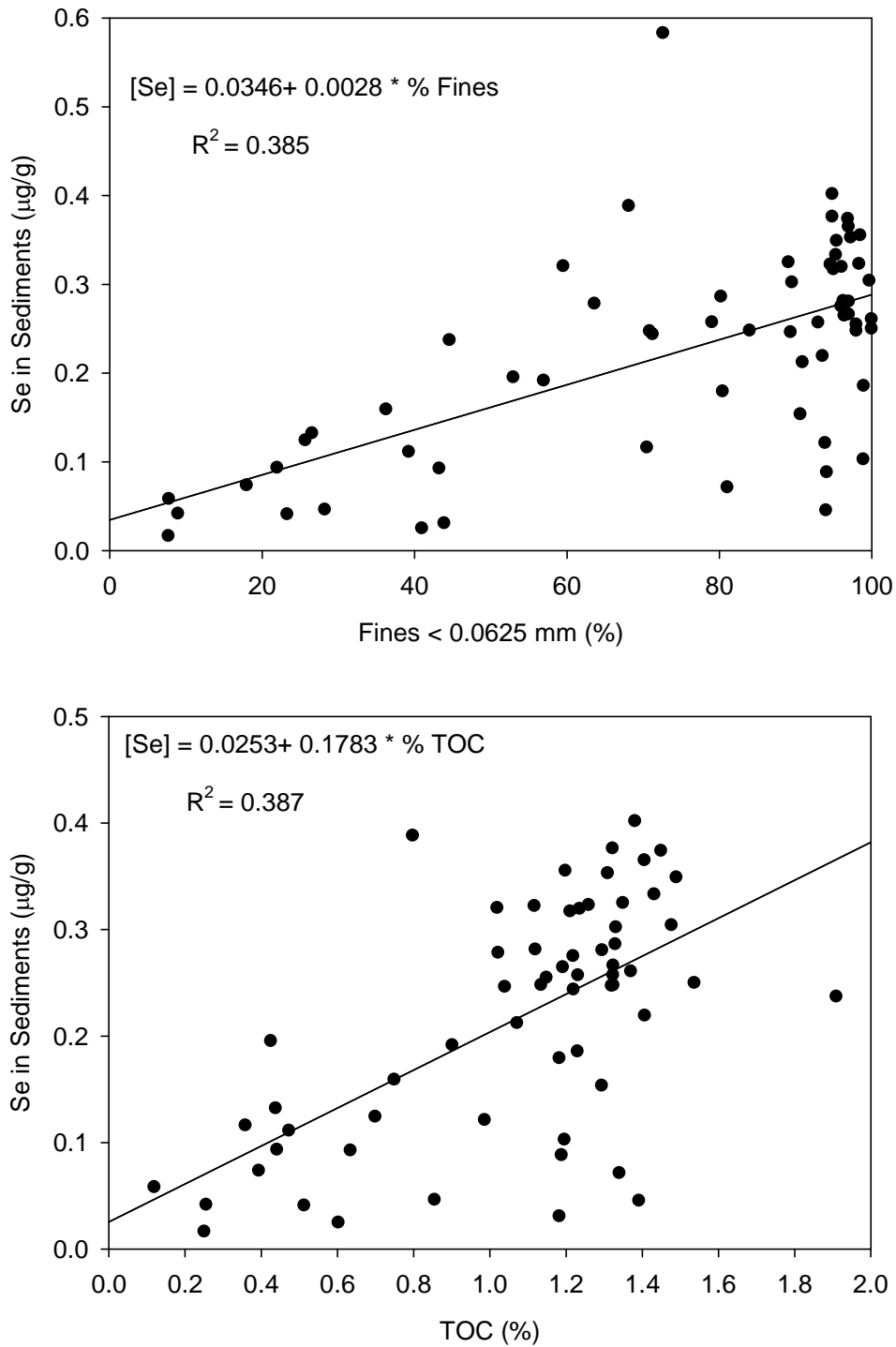


Figure 2-25 Relationship between selenium concentrations in sediments and sediment characteristics at random sampling sites (data source: RMP).

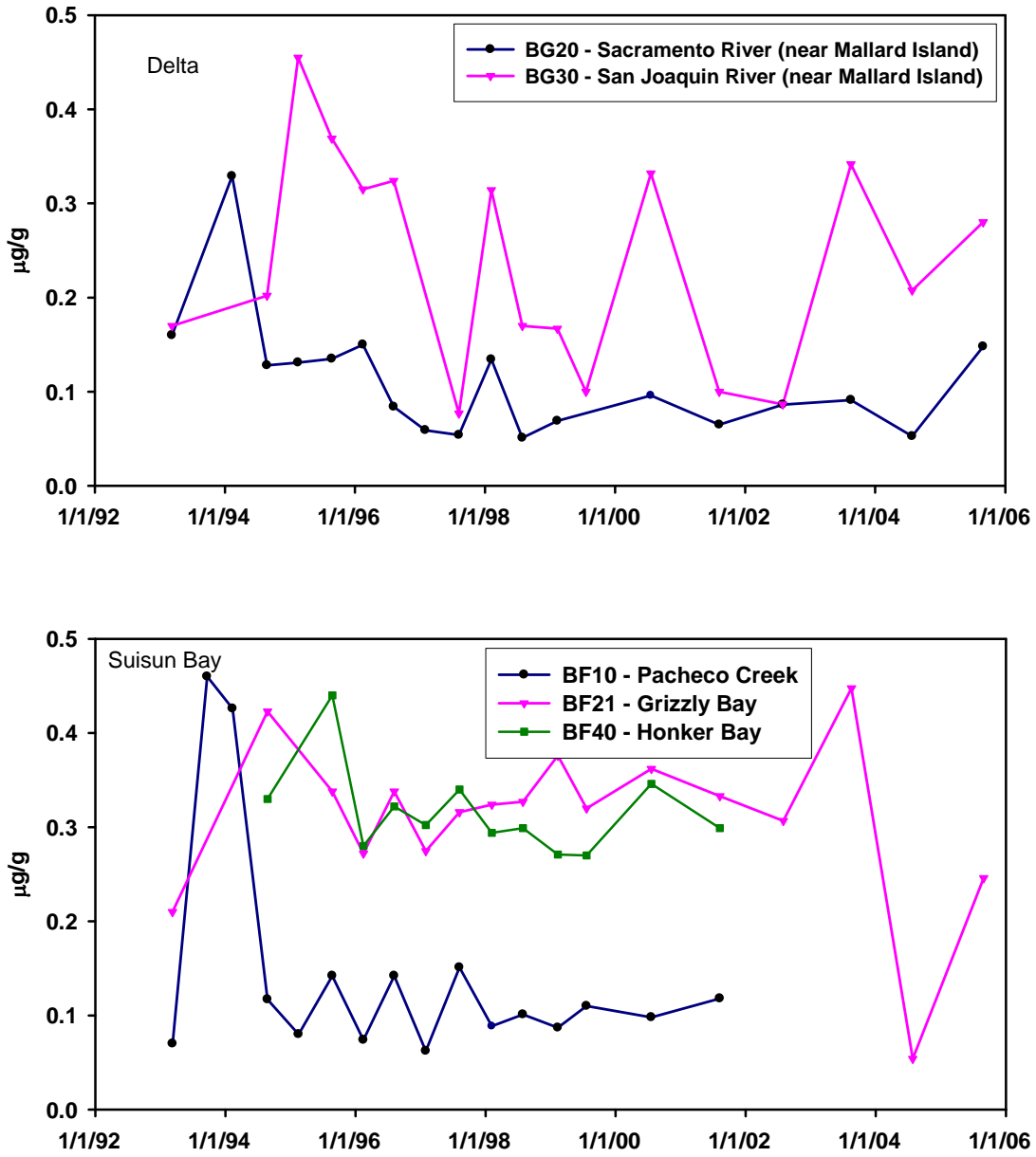


Figure 2-26 Selenium concentrations in sediments as a function of time in stations near Mallard Island and in Suisun Bay (data source: RMP).

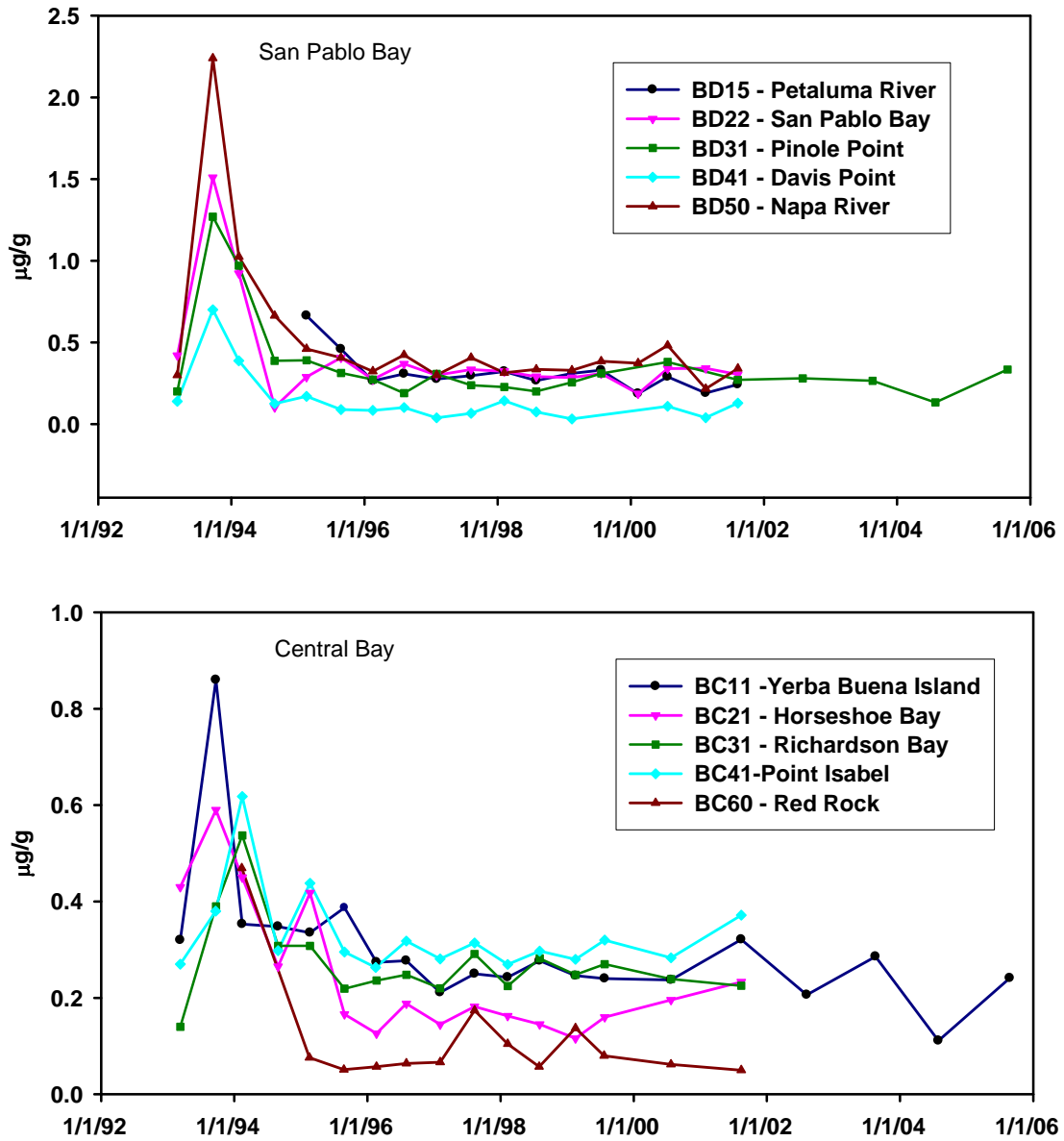


Figure 2-27 Selenium concentrations in sediments as a function of time in San Pablo and Central Bay (data source: RMP).

3. SOURCE CHARACTERIZATION

The goal of the source characterization is to quantify the various point and non-point sources that contribute selenium to North San Francisco Bay. The sources evaluated and their key features are listed below.

- Atmospheric deposition – includes both dry and wet deposition to the bay water surface, and is usually considered as a small selenium source
- Urban and non-urban runoff from local tributaries – includes both agricultural and urban stormwater runoff, and may be a significant source of selenium during the wet season
- Delta inflow – which consists of flow from both the San Joaquin and Sacramento Rivers, is the major source of selenium to the bay
- Municipal wastewater effluents – which generally have low concentrations of selenium
- Petroleum refineries – which were the major sources of selenium (in the form of selenite) in the 1980's and have decreased dramatically since 1999 because of improved wastewater treatment
- Input from bay sediment – net sediment erosion, resuspension, diffusion, and dredging activities can be potential internal sources of selenium to the bay water column

The magnitudes of the selenium loads associated with these sources are discussed in the subsequent sections. The dry season is a critical period for selenium bioaccumulation due to longer residence time, while wet season has larger flow volumes and can potentially contribute larger loads of selenium to the Bay. Therefore, for source categories with available flow information, both dry and wet season loads were calculated and compared. The relative contribution of loads may vary significantly between the dry and wet seasons.

3.1. OVERVIEW OF PREVIOUS SOURCE ESTIMATES

Presser and Luoma (2006) estimated annual selenium loads from San Joaquin River at Vernalis to be 1,614 – 7,819 kg/yr with an average of 4,440 kg/yr for the years of 1986-1998. Selenium loads from five agricultural sub-areas of western San Joaquin Valley were also estimated under different discharging scenarios by Presser and Luoma (2006).

Of special relevance to any long-term evaluation of selenium trends in NSFB is the reduction of loads from refineries that occurred because of major improvements in wastewater treatment in the late 1990s. Selenium loadings from oil refineries ranged between 928-2,116 kg/yr during 1987 and 1988 (Cutter and San Diego-McGlone, 1990) and 1,415-3,400 kg/yr during 1986-1992 (SFBRWQCB, 1993). Refinery discharge declined after July 1998 and selenium loads from five refineries were estimated to be 506 kg/yr in 1999 (Presser and Luoma, 2006).

Loads from the Sacramento River were calculated using an average concentration of 0.04 µg/L as a conservative estimate and were estimated to be 247 kg/yr during a critically dry

year, 494 kg/yr for dry to critically dry year, 839 kg/yr for a median year and 1579 for a wet year (Presser and Luoma, 2006).

Abu-Saba and Ogle (2005) developed a conceptual model for selenium in the bay and estimated various sources including:

- Riverine fluxes via the Delta
- North Bay refinery effluent discharges
- Municipal wastewater, local tributaries, and urban runoff

Loading rates from the Delta were estimated by multiplying net freshwater discharge from the Delta and a “river end member concentration” estimated by flow weighting concentrations at the Sacramento and San Joaquin Rivers, measured by Cutter and Cutter (2004). Estimated loading rates from the Delta by Abu-Saba and Ogle (2005) for the period of November 1997–November 1999 were 282–9,570 kg/yr for dissolved selenium, and 47–686 kg/yr for particulate selenium. Oil refinery effluent discharge loading was calculated from effluent flow rates and selenium concentrations reported by Cutter and Cutter (2004) and ranged between 204–552 kg/yr. Urban and non-urban runoff and municipal wastewater loadings were estimated by some simple calculations (Abu-Saba and Ogle, 2005). Average annual runoff volume (both urban and non-urban) for the Bay Area is about 900 Mm³ (McKee et al., 2002) and annual discharge volume from wastewater is at a similar volume of 866 Mm³ (Grovhoug et al., 2004). Selenium concentration in local runoff and municipal wastewater effluents were thought to range from 0.1–1 µg/L, therefore Abu-Saba and Ogle (2005) estimated loadings from each of these sources to range between 90–900 kg/yr with uncertainty.

Cutter and Cutter (2004), based on data for five sampling events in 1997, 1998, and 1999, estimated riverine inputs from the Delta into the bay and inputs from refineries to the bay. Riverine inputs of dissolved selenium ranged between 773–26,195 g/day, with selenite inputs ranging between 110–2,446 g/day, selenate ranging between 497–17,121 g/day, and organic selenide ranging between 55–6,486 g/day. Refinery loadings were estimated to range between 1,515–6,328 g/day with selenite ranging between 379–2,414 g/day, selenate between 970–2,107 g/day and organic selenide ranging between 174–1,854 g/day. These data are described in daily load terms, as in the original work; the analysis below uses this information to compute annual loads. Because of the variability in daily flows and loads, the daily loads cannot be converted to annual loads simply by multiplying by 365. The computation needs assumptions or data on daily flows, as described for the load calculations performed in the current study.

Subsequent sections present load estimates for all significant non-point and point-sources. These analyses build on previous work and include consideration of the most recent data, especially for point sources, tributaries, and the Delta.

3.2. DIRECT ATMOSPHERIC DEPOSITION

Atmospheric deposition of selenium occurs both as dry and wet forms. Selenium is emitted to the atmosphere naturally as volatile dimethyl selenide, or as selenium dioxide and

elemental selenium from fossil fuel combustion (Cutter and Church, 1986). Deposition of selenium is part of a global cycle as gaseous selenium bound to particulate materials can be transported over long distances (EPA, 2002). Selenium in wet deposition consists of selenate, selenite, and elemental selenium. Rainwater samples from coastal California indicated that selenite is the major species in wet deposition for the region (Cutter, 1978). Dry deposition of selenium is mainly associated with fine particles ($< 1 \mu\text{m}$; Duce et al. 1976; Sweet et al. 1998) and gaseous forms.

Dry and wet deposition of selenium has not been measured in the San Francisco Bay and estimates were made using data from other studies. Atmospheric deposition of selenium is believed to represent only a small input to the water surface and the watershed in other studies (EPA, 2002). Reported concentrations of selenium in precipitation are 0.1 - 0.4 $\mu\text{g/L}$ in urban areas (Mosher and Duce, 1989). Concentrations in precipitation measured in the Chesapeake Bay atmospheric deposition study are in the range of 0.07 - 0.17 $\mu\text{g/L}$ (EPA, 1996). To estimate the significance of wet deposition, a simple calculation was done by extrapolating concentrations in the literature to the North Bay. Given an approximate annual rainfall of 450 mm/yr (McKee et al. 2003) and a water surface of 434 km^2 in the North Bay, direct wet deposition of selenium is in the range of 13.7 - 78.1 kg/yr (assuming selenium concentrations of 0.07-0.4 $\mu\text{g/L}$). Wet deposition of selenium is relatively bioavailable as selenite is the major species.

Dry deposition was calculated from air-phase concentrations of selenium. Reported concentrations in the air exhibit a large variation from 0.3 to 2.4 ng/m^3 . Concentrations measured in the Chesapeake Bay range from 1.4 - 1.8 ng/m^3 (EPA, 1996). Different deposition velocity values have been used to estimate dry deposition fluxes for the Great Lakes (0.1 cm/s, Sweet et al. 1998) and the Chesapeake Bay (0.26 cm/s low, 0.72 cm/s high, EPA, 1996). Selenium in the air is mostly associated with fine particles; therefore a lower deposition velocity is expected. Based on a concentration range of 0.3 - 2.4 ng/m^3 and deposition velocities of 0.1 cm/s and 0.26 cm/s, estimated dry deposition is in the range of 4.1 - 85.4 kg/yr.

Due to the lack of site-specific measurements of selenium deposition in the bay, the simple extrapolations from other sites are associated with large uncertainties. Nonetheless, these estimates provide a reference for comparison with other sources discussed below.

3.3. URBAN AND NON-URBAN STORMWATER RUNOFF FROM LOCAL TRIBUTARIES

Local tributaries, that is, streams that discharge directly into the North Bay and not into the Delta and/or the Sacramento and San Joaquin Rivers, can contribute elevated pollutant loadings due to the presence of urban and agricultural lands in their watersheds. Although local tributaries are only responsible for about 4% of the runoff to the bay, they were found to have a much higher sediment export rate than the Central Valley ($\sim 100 \text{t/km}^2$ vs. $\sim 14 \text{t/km}^2$; McKee et al. 2003). With respect to selenium, relatively high selenium concentrations have been measured in tributaries around the Bay area, both in the wet and dry seasons. Total recoverable selenium concentrations observed in several watersheds in the South Bay during 2005-2006 ranged between 0.22-1.7 $\mu\text{g/L}$ (median 0.38 $\mu\text{g/L}$) for the dry season and 0.56-9 $\mu\text{g/L}$ (median 3.6 $\mu\text{g/L}$) for the wet season (EOA, 2006). Selenium concentrations observed in five tributaries of the North Bay in the Surface Water Ambient Monitoring

Program (SWAMP) study in 2001-2002 suggested high concentrations of 0.18-3.39 $\mu\text{g/L}$ (median 0.94 $\mu\text{g/L}$) during the dry season and 0.39- 3.14 $\mu\text{g/L}$ (median 0.90 $\mu\text{g/L}$) during the wet season (SFBRWQCB, 2007a). Total selenium concentrations as high as 1.7 $\mu\text{g/L}$ and 4 $\mu\text{g/L}$ during wet and dry seasons of 2003 -2004 were observed in the Petaluma River (SFBRWQCB, 2007b). Selenium observed in the tributaries is mostly in the dissolved form. Little information is available on the speciation or bioavailability of selenium from local tributaries.

3.3.1 Review of Selenium Concentration Data in Tributaries

Selenium concentrations in local tributaries monitored for the SWAMP⁴ study by the San Francisco Bay Regional Water Quality Control Board during 2001-2004 are listed in Table 3-1. SWAMP monitoring programs targeted both clean and polluted areas of the watershed. Therefore, many sampling sites are located in urban or agricultural areas. For each watershed, a number of stations along the tributaries were monitored with 2-4 stations measured for selenium. Among the watersheds monitored, Wildcat Creek/San Pablo Creek and Suisun Creek were sampled during 2001- 2002. Kirker Creek, Mt. Diablo Creek and Petaluma River were sampled during 2003-2004. Three sampling events based on hydrological conditions were targeted for each monitoring year including wet (January to March), spring (April to May) and dry (June to October). Samples were analyzed for both total and dissolved selenium with a minimum detection limit (MDL) of 0.1 $\mu\text{g/L}$ (SFBRWQCB, 2007b).

Relatively high total selenium concentrations were found for all seasons (Figure 3-1). The highest total selenium concentration was observed at an urban influenced site during the dry season (8.1 $\mu\text{g/L}$ at KIR115-Kirker Creek Apartments). Average total selenium concentrations for the most downstream sites of all the North Bay watersheds are 1.57 $\mu\text{g/L}$ for wet season, 1.03 $\mu\text{g/L}$ for spring season and 1.95 $\mu\text{g/L}$ for dry season (Table 3-1). The downstream sites were considered to be more representative of the watershed condition by integrating all the land uses and therefore only downstream sites were used in the calculations of loads to the bay. Note that the 8.1 $\mu\text{g/L}$ value did not factor in the average because it was not the most downstream value on Kirker Creek. Due to the limited number of samples, for some sampling events, higher dissolved than total selenium concentrations were reported. For the purpose of the load calculations, estimates were made using total selenium concentrations.

The Bay Area Stormwater Management Agencies Association (BASMAA) has also sampled selenium concentrations from some local tributaries around the North Bay during 1988-1995 (BASMAA, 1996). The sampling sites for the North Bay are mostly located in the Alameda County with two sites located in the Contra Costa County. Selenium concentrations reported by BASMAA are lower than values reported in subsequent SWAMP studies (Figure 3-2). Variable detection limits are noted for the BASMAA dataset, with higher detection limit (at 0.2 $\mu\text{g/L}$) and higher percentage of non-detects in early period of the study (1988-1992). Lower detection limits (generally below 0.05 $\mu\text{g/L}$) were used for latter period of the study and most of the samples were above detection limits. Measured concentrations seem to vary

⁴ Surface Water Ambient Monitoring Program, a statewide program to assess water quality conditions in surface water bodies.

with detection limits. Land uses for watersheds surrounding the sampling locations include open forests, industrial, residential and commercial. Median concentrations are 0.40 $\mu\text{g/L}$ during dry weather ($n = 7$) and 0.33 $\mu\text{g/L}$ for storm event sampling ($n = 28$). By land use, median concentrations are 0.29 $\mu\text{g/L}$, 0.35 $\mu\text{g/L}$ and 0.30 $\mu\text{g/L}$ for residential, open and industrial sites. For some of the BASMAA sampling sites, monitoring was continued for multiple years.

Table 3-1
Total and dissolved selenium concentrations observed at the SWAMP sites during wet, spring and dry seasons. Data for the most downstream location on each stream are shown. Data are individual values.

Creek	Site	Season	Year	Total $\mu\text{g/L}$	Dissolved $\mu\text{g/L}$
Kirker Creek	KIR020	Wet	2003-2004	1.26	1.21
		Spring	2003-2004	1.30	1.00
		Dry	2003-2004	2.50	2.00
Mt. Diablo Creek	MTD010	Wet	2003-2004	2.00	2.00
		Spring	2003-2004	0.40	0.30
Petaluma River	PET010	Wet	2003-2004	1.30	1.40
		Spring	2003-2004	0.20	0.50
	PET310	Wet	2003-2004	1.70	1.80
		Spring	2003-2004	1.30	1.50
		Dry	2003-2004	4.00	3.90
San Pablo Creek	206SPA020	Spring	2001-2002	2.74	2.57
		Dry	2001-2002	1.60	1.53
Suisun Creek	207SUI010	Spring	2001-2002	0.90	1.04
		Dry	2001-2002	0.32	0.17
Wildcat Creek	206WIL020	Spring	2001-2002	0.39	1.41
		Dry	2001-2002	1.33	1.11
Average		Wet		1.57	1.60
		Spring		1.03	1.19
		Dry		1.95	1.74

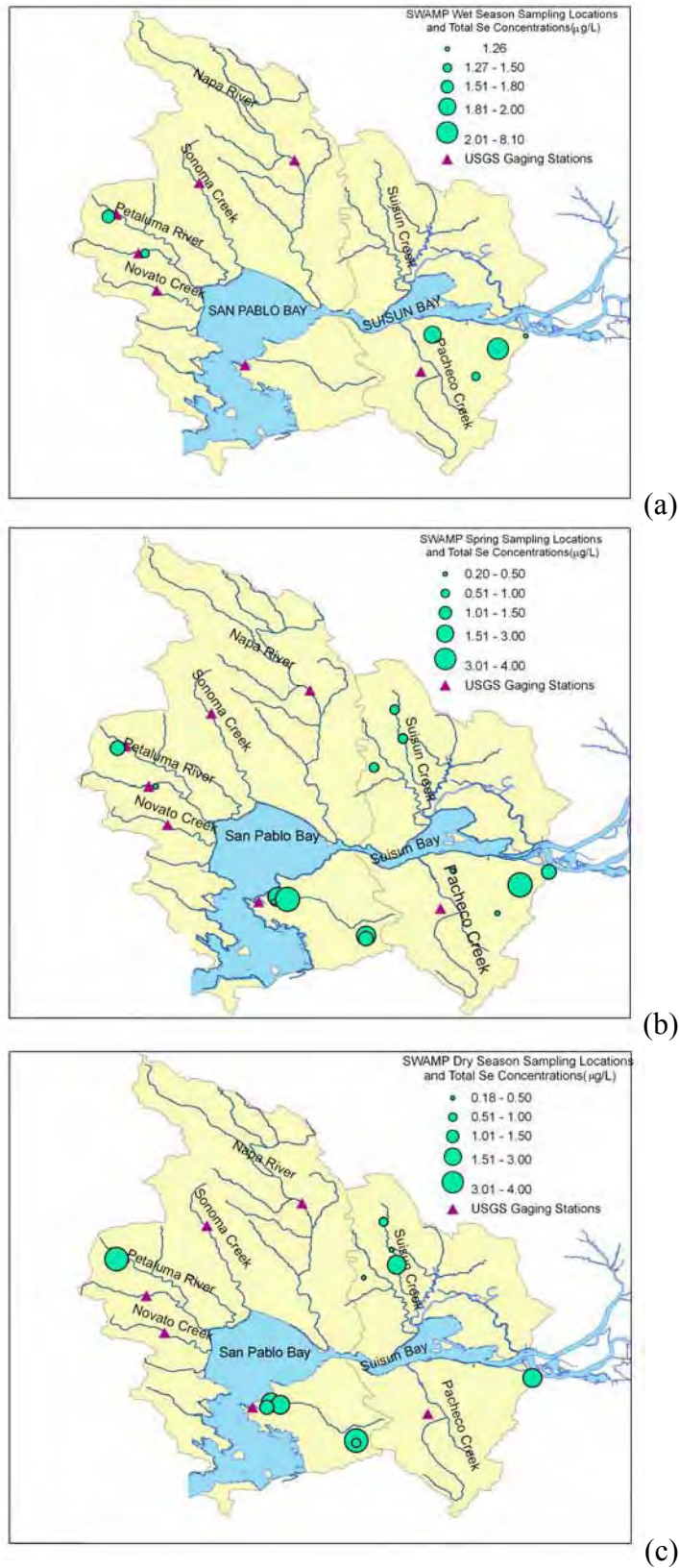


Figure 3-1 Total selenium concentrations in the wet (a), spring (b) and dry (c) seasons in local tributaries of the North Bay, sampled in the SWAMP program.

Three methods were used to estimate selenium loads from local tributaries based on two different methods of estimating runoff from local watersheds and selenium concentration data from SWAMP and BASMAA study.

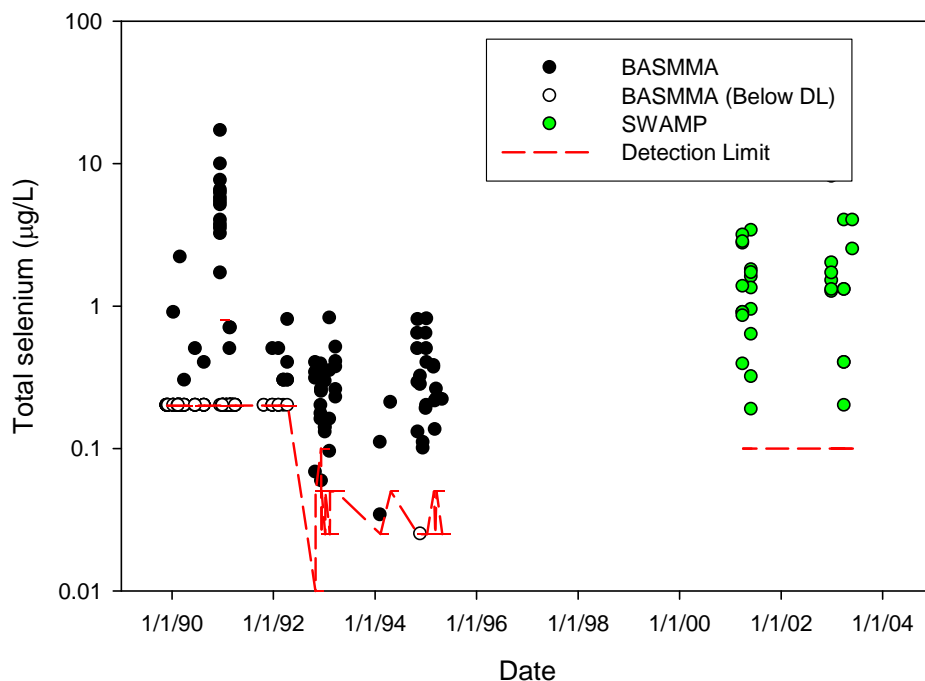


Figure 3-2 Total selenium concentrations in tributaries of NSFB sampled during 1990–1996 and 2000–2003 (Source: BASMAA, 1996; SWAMP data from SFBRWQCB, 2007a, b).

3.3.2 Method 1: Modeled Estimates of Runoff in Tributaries and Using SWAMP Concentrations

Total annual runoff from local watersheds has been computed using a simple model by Davis et al. (2000). The predicted runoff compared reasonably well to the limited observed data ($r^2 = 0.62-0.89$). We used the Davis et al. (2000) runoff estimates and concentrations measured in the SWAMP study to estimate loadings from each of the watersheds surrounding the North Bay (Table 3-2). A map of these local watersheds (hydrological areas) is shown in Figure 3-3. The average annual loadings of total selenium from local tributaries to the North Bay were estimated to be 913.9 kg/yr, with the Napa River and Fairfield watersheds being the largest sources. Higher selenium loads from these watersheds are most likely due to larger watershed areas and high annual runoff.

Runoff in the Bay area shows large year-to-year variation. Therefore, loadings from local tributaries are expected to vary greatly with climate conditions. Watersheds in the Bay area show inter-annual variation with coefficient of variation (C/V) ranging from 0.65 to 1.01 (McKee et al. 2002). The 10th and 90th percentiles of rainfall in the Bay area for the record period of 1961-1990 were summarized previously in Davis et al. (2000). Assuming constant runoff concentrations under different climate conditions, 10th and 90th percentiles of the selenium loadings were calculated to be 522.8 kg/yr and 1367.2 kg/yr, respectively.

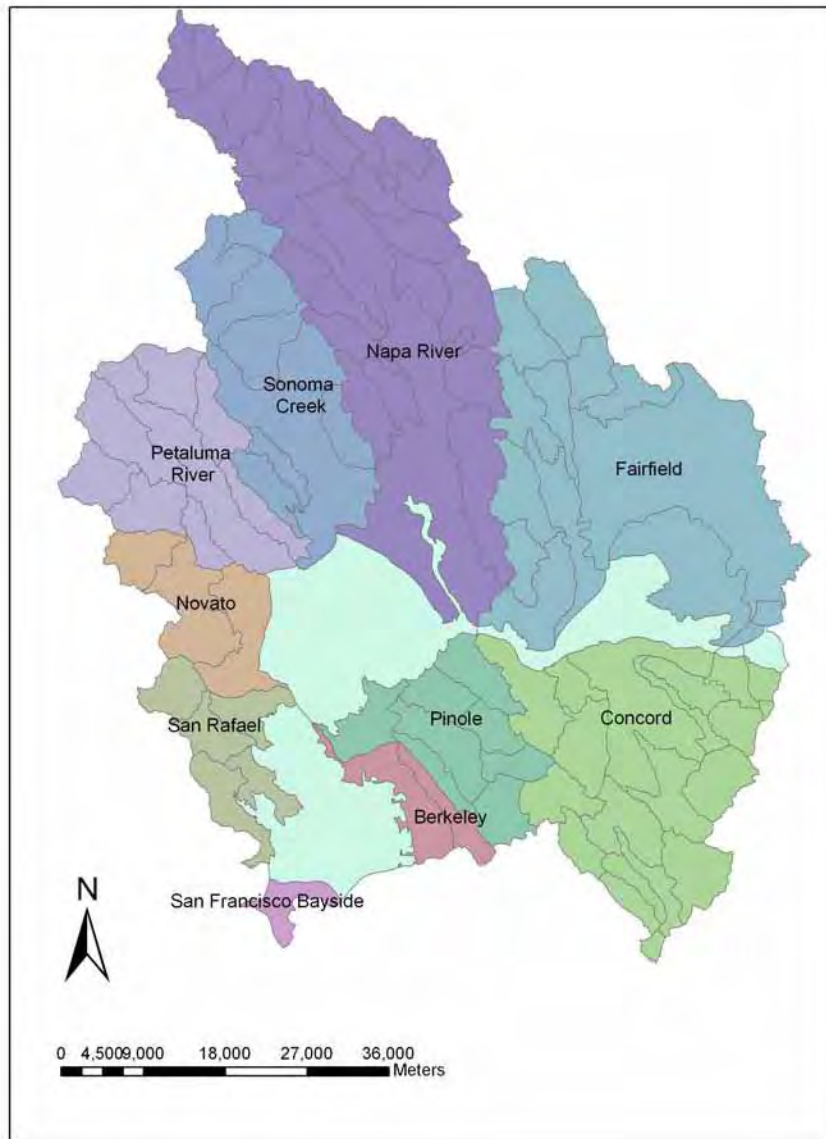


Figure 3-3 Hydrological areas surrounding NSFB. Source: San Francisco Estuary Institute

Table 3-2
Runoff and selenium loadings from local watersheds to the North Bay

Hydrologic Area	Total Annual Runoff (Mm ³ /yr) ¹	SWAMP Sampling Station	Mean total selenium concentrations (µg/L) ²	Total selenium loadings (kg/yr)
San Rafael	56		1.57	87.6
Berkeley	25		1.57	39.1
San Francisco-Bayside	8.8		1.57	13.8
Novato	47		1.57	73.6
Petaluma River	60	Petaluma River	1.5	90
Sonoma Creek	68		1.57	106.4
Napa River	180		1.57	281.7
Pinole	35	Wildcat, San Pablo	1.57	54.8
Fairfield	129	Suisun Creek	0.9	116.1
Concord ³	106	Mt. Diablo Creek	0.4	42.4
Concord ⁴	6.7	Kirker Creek	1.26	8.4
Total	721.5			913.9

¹Davis et al. (2000)

²SFBRWQCB (2007a, b), 1.57 µg/L is the wet season mean concentration for all the most downstream sites in the North Bay watersheds sampled (n = 4).

³Subunits of the Concord hydrologic area (ID: 220731, 220732, and 220733)

⁴A subunit of the Concord hydrologic area (ID: 220734)

3.3.3 Method 2: Measured Flow in Selected Tributaries and Using SWAMP Concentrations

The second method is based on USGS flow data in the Bay area to estimate selenium loading from local tributaries. Daily flow records from several USGS gaging stations for some major North Bay tributaries are available for different periods (Table 3-3 and Table 3-4). Long-term average monthly flow at these stations suggested that the majority of the flow is discharged during the wet season (defined as Oct 1st to Apr 30th). Flow during the dry season (defined as May 1st to September 30th) comprises only a very small portion of the wet season flow (0.2 – 3.5%) except Walnut Creek (13.1%) and Pinole Creek (5.8%). Many of the stations have relatively short flow records and contain values prior to 1990. Flow records at these stations may not fully reflect the current hydrologic regime of the watershed.

The long-term average monthly flow and the seasonal concentrations measured by the SWAMP study were used to estimate long-term average selenium loadings at these gaging stations for each month. Loadings were estimated by multiplying flow and concentrations of the same river. For tributaries without observed selenium concentrations, the overall average concentration for all the North Bay downstream sites was used. The estimated loadings are shown in Figure 3-4. Following the pattern in flow volumes, total selenium is mainly delivered to the bay in wet season. Dry season loadings average 0.2 – 3.0% of wet season loadings for 6 of the 8 stations (Table 3-5). An annual areal loading was also estimated for

each of the tributary, based on total annual selenium loading and the drainage area. The estimated areal loadings were used to scale up loading estimates of the entire hydrological area (e.g. Novato Creek at Novato was scaled up for the whole Novato hydrological area). For hydrological areas without data (e.g., San Rafael), areal loading from a nearby watershed was used.

Estimated total selenium loadings for the North Bay area by hydrological area are summarized in Table 3-6 and Figure 3-5. Total selenium loadings from local tributaries using the method above were estimated to be 1,511 kg/yr, higher than the estimates from Method 1. A large portion of the loadings were estimated to originate from Napa and Sonoma hydrological areas. Due to the lack of selenium concentrations for these two areas in the SW AMP dataset, an overall mean concentration of the whole North Bay tributaries were used and therefore the estimates are subject to large uncertainty. Flow records for the Napa and Sonoma rivers also suggested higher runoff from these two areas compared to the rest of the North Bay (337 and 422 mm/yr for Napa and Sonoma, compared to ~200 mm/yr for the other tributaries), contributing to the high estimated selenium loadings.

Table 3-3
Major USGS gaging stations in North Bay watersheds (Source: USGS)

Station Name	Station Number	Latitude	Longitude	Drainage Area (mi ²)	Flow Period
Novato Creek at Novato	11459500	38 06'28"	122 34'44"	17.6	1946-current
San Antonia Creek Nr Petaluma	11459300	38 10'57"	122 36'55"	28.9	1975-1981
Petaluma River at Petaluma	11459000	38 15'40"	122 39'35"	30.9	1948-1963
Sonoma Creek at Agua Caliente	11458500	38 19'24"	122 29'36"	58.4	1955-current
Napa River nr. Napa	11458000	38 22'06"	122 18'08"	218	1929-current
Wildcat Creek at Richmond	11181400	37 57'41"	122 21'33"	8.69	1964-1975
Walnut Creek at Concord	11183600	37 56'43"	122 02'55"	85.2	1968-1992
Pinole Creek at Pinole	11182100	37 58'21"	122 14'43"	10	1938-1977

Table 3-4
Long-term average monthly flow (in cfs) at USGS gaging stations in North Bay watersheds for the record period (Source: <http://waterdata.usgs.gov/nwis>)

	USGS114 59500 (Novato Creek at Novato)	USGS114 59300 (San Antonia Creek nr. Petaluma)	USGS1145 9000 (Petaluma River at Petaluma)	USGS11 458500 (Sonoma Creek at Agua Caliente)	USGS11 458000 (Napa River nr. Napa)	USGS1118 1400 (Wildcat Creek at Richmond)	USGS1118 3600 (Walnut Creek at Concord)	USGS11 182100 (Pinole Creek at Pinole)
Jan	46.79	82.47	58.75	244.85	695.67	22.06	112.55	11.97
Feb	46.56	70.48	64.11	216.32	710.04	11.78	132.28	11.23
Mar	26.92	30.69	28.38	124.3	486.98	10.09	108.15	7.94
Apr	10.50	5.35	14.00	70.74	198.32	6.20	52.33	5.44
May	1.65	0.72	0.49	16.44	59.26	0.89	19.13	1.23
Jun	0.82	0.17	0.03	5.12	18.46	0.61	12.32	0.59
Jul	0.66	0	0	1.81	5.72	0.27	9.52	0.29
Aug	0	0	0	0.98	2.51	0.01	8.27	0.16
Sep	0	0	0	0.77	1.95	0.03	8.77	0.13
Oct	0.69	0.01	0.96	6.28	10.26	1.01	14.33	0.53
Nov	3.01	0.63	2.24	24.26	68.85	4.06	32.47	0.53
Dec	16.81	13.84	37.69	159.32	335.17	7.73	52.05	3.81
Dry season (cfs)	3.9	0.9	0.5	25.1	87.9	1.8	58.0	2.4
Wet season (cfs)	151.3	203.5	206.1	846.1	2505.3	62.9	504.2	41.5
Dry as wet %	2.59	0.45	0.25	2.97	3.51	2.88	11.51	5.79
Runoff (mm/yr)	249.8	200.3	189.4	422.5	336.9	211.0	186.9	124.2

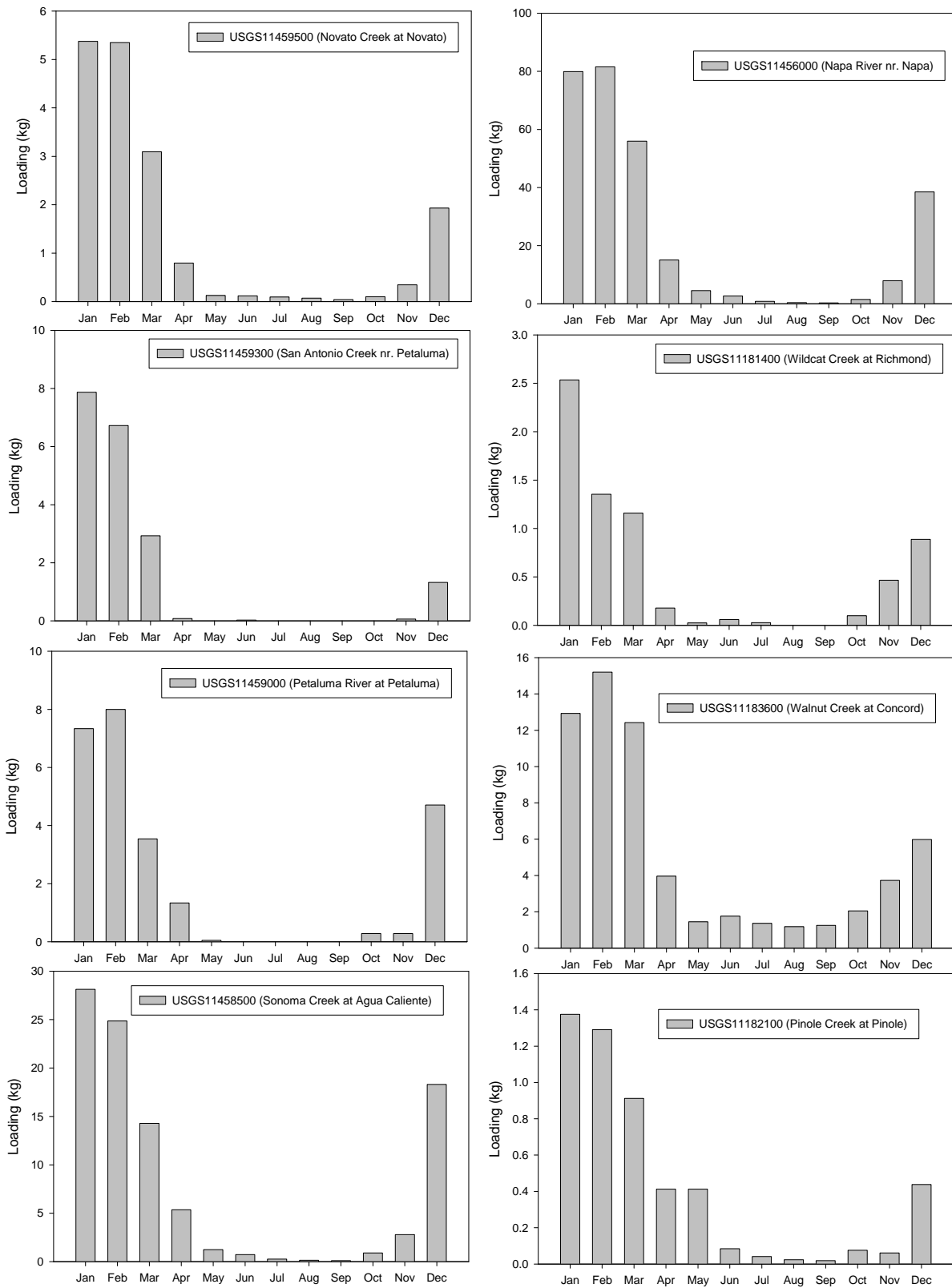


Figure 3-4 Estimated long-term average monthly selenium loadings at gaging stations of local tributaries.

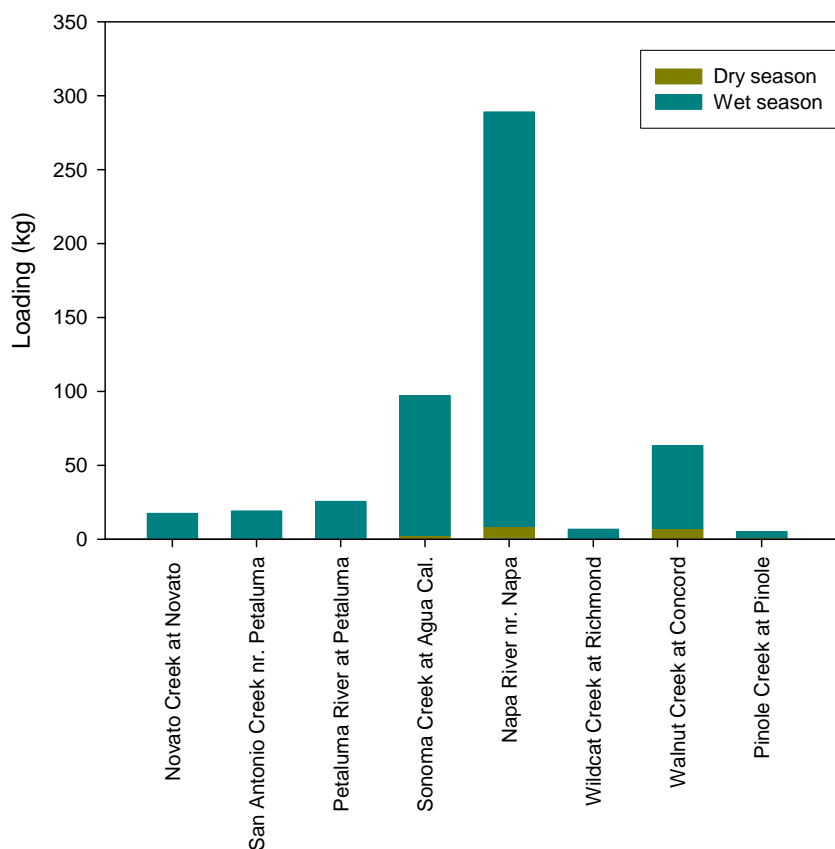


Figure 3-5 Comparison of dry and wet season selenium loadings for tributaries in the North Bay.

Seasonal selenium concentrations from the SWAMP data set were also used in conjunction with the daily flow at Napa River near Napa to estimate daily selenium loadings for 1991-2007. The estimated daily loadings were accumulated to estimate seasonal loading for all the years. As a result of variations in hydrological conditions, total selenium loading in Napa River near Napa vary largely across the years (Figure 3-6). Total selenium loadings can be greater than 700 kg/yr during wet year (1995) versus less than 100 kg/yr during a dry year (1994). The dry and wet year notation was based on the classification system for San Joaquin and Sacramento River by the Department of Water Resources (<http://cdec.water.ca.gov/cgi-progs/iodir/WSIHIST>). Wet and above normal years are classified as wet years. Dry, below normal and critically dry years are classified as dry years. Dry season is defined as May 1st to September 30th. The wet season is defined as October 1st to April 30th.

Table 3-5
Estimated long-term average monthly total selenium loadings (kg/month) to the gaging stations.

	USGS114 59500 (Novato Creek at Novato)	USGS114 59300 (San Antonia Creek nr. Petaluma)	USGS114 59000 (Petaluma River at Petaluma)	USGS114 58500 (Sonoma Creek at Agua Caliente)	USGS114 58000 (Napa River nr. Napa)	USGS11181 400 (Wildcat Creek at Richmond)	USGS11118 3600 (Walnut Creek at Concord)	USGS11 182100 (Pinole Creek at Pinole)
Jan	5.37	7.87	7.33	28.13	79.92	2.53	12.93	1.38
Feb	5.35	6.73	8.00	24.85	81.57	1.35	15.20	1.29
Mar	3.09	2.93	3.54	14.28	55.94	1.16	12.42	0.91
Apr	0.80	0.08	1.34	5.36	15.04	0.18	3.97	0.09
May	0.13	0.01	0.05	1.25	4.49	0.03	1.45	0.41
Jun	0.12	0.02	0.01	0.73	2.64	0.06	1.76	0.08
Jul	0.09	0.00	0.00	0.26	0.82	0.03	1.36	0.04
Aug	0.07	0.00	0.00	0.14	0.36	0.00	1.18	0.02
Sep	0.04	0.00	0.00	0.11	0.28	0.00	1.26	0.02
Oct	0.10	0.00	0.28	0.90	1.47	0.10	2.05	0.08
Nov	0.35	0.06	0.28	2.79	7.91	0.47	3.73	0.06
Dec	1.93	1.32	4.70	18.30	38.50	0.89	5.98	0.44
Annual total (kg/yr)	17.4	19.0	25.5	97.1	288.9	6.8	63.3	4.8
Areal loading (kg/mi ²)	0.99	0.66	0.83	1.66	1.33	0.78	0.74	0.48
Dry season (kg)	0.45	0.04	0.06	2.49	8.59	0.12	7.01	0.26
Wet season (kg)	16.99	18.99	25.47	94.61	280.35	6.68	56.28	4.56
Dry as wet %	2.65	0.21	0.22	2.63	3.06	1.73	12.46	5.71

Table 3-6
Estimated annual total selenium loadings for the hydrological areas in the North Bay.

Hydrological Areas	Drainage Area (Mm ²)	Area (mi ²)	Loadings (kg/yr)	Dry (kg)	Wet (kg)
Novato	183.98	71.03	70.4	1.8	68.6
San Rafael	157.66	60.87	60.3	1.6	58.8
San Francisco Bayside	28.76	11.11	11.0	0.3	10.7
Berkeley	87.59	33.82	26.4	0.4	26.0
Pinole	152.43	58.85	28.4	1.5	26.9
Concord	648.27	250.30	185.9	20.6	165.3
Fairfield	877.89	338.96	251.8	27.9	223.9
Napa	937.89	362.12	480.0	14.3	465.7
Sonoma	429.77	165.93	275.9	7.1	268.6
Petaluma	377.64	145.81	120.5	0.3	120.2
Total			1510.6	75.8	1434.8

Total Selenium Loading in Napa River nr. Napa

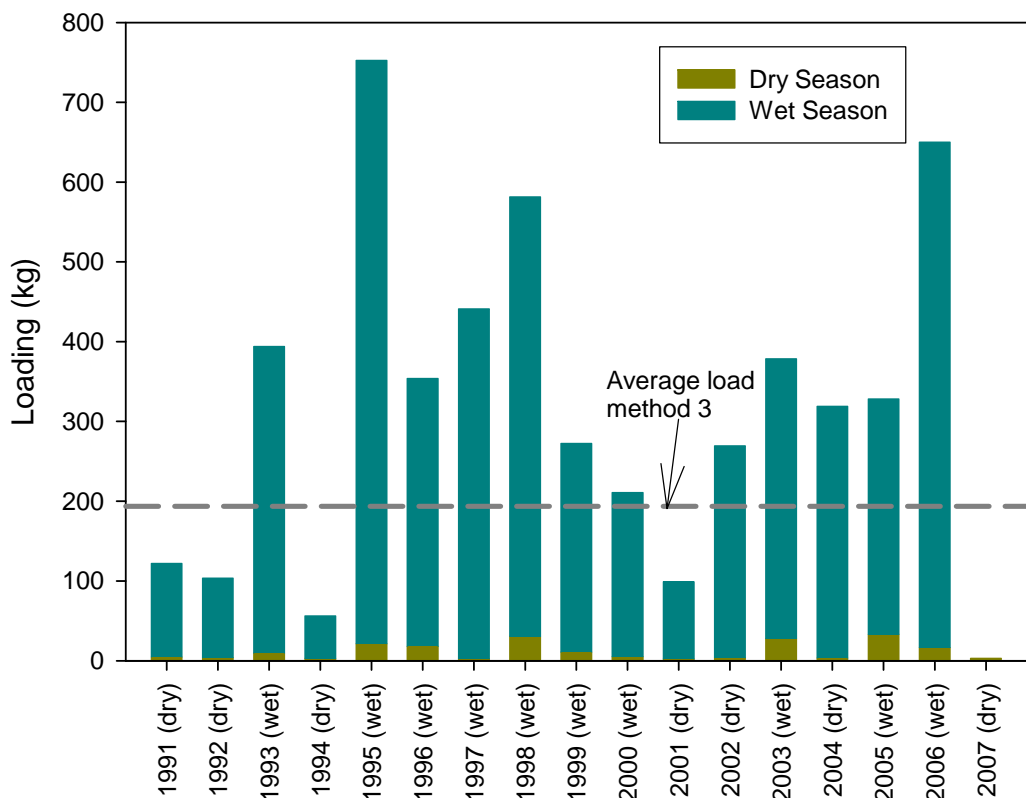


Figure 3-6 Dry and wet season selenium loadings by water year at Napa River near Napa.

3.3.4 Method 3: Modeled Estimates of Runoff with BASMAA and SWAMP concentrations for Calculating Land Use-Specific Loads

To estimate storm water loads of selenium from urban areas, a previously published approach was used (Davis et al., 2000). This approach has been used in estimating urban loads of PCBs in the San Francisco Bay PCB TMDL (KLI, 2002; SFBRWQCB, 2007c). Loads are estimated from five broad categories of land use (agricultural, open space, industrial, commercial and residential) based on estimated runoff from each land use type and land-use specific concentrations. Urban lands are defined as a group and include industrial, commercial and residential lands.

Land uses for each hydrological area were previously determined by Davis et al. (2000; Table 3-7). Best estimates of runoff coefficient for each land use type were also derived by Davis et al. (2000; Table 3-7). KLI (2002) sampled stormwater concentrations of PCBs and Hg in the Bay area, however selenium was not sampled in this effort. For selenium, land use specific concentrations were derived from BASMAA (1996) and SWAMP study (SFBRWQCB 2007a, b). BASMAA (1996) sampling stations include sites that are mostly residential and sites that are more dominated by forests/open area. Therefore, overall mean concentrations for sites with dominant land use of residential, open, and industrial were calculated. Concentrations for agricultural land use were assumed to be the same as open area. When concentrations were reported as below detection limits, half of the detection limit was used. Mean selenium concentrations from the BASMAA study are similar across land uses (Table 3-8). Stations from the SWAMP study are generally located in the urban areas, with Suisun Creek stations located in agriculture-dominated areas. Therefore values from Suisun Creek were used to derive concentrations for the agricultural areas. Due to the differences in concentrations reported in two programs, values from BASMAA were used as lower bound of concentrations from local tributaries, while SWAMP data were used as an upper bound (Table 3-8). Overall, Method 3 results in a somewhat lower estimate of loads than the prior two methods, with loads ranging from 354.3 to 838.7 kg/yr.

Table 3-7
Summary of drainage areas and land use for each hydrologic area of NSFB
(Davis et al. 2000; KLI, 2002)

Hydrological areas (HA)	Drainage Area (Mm ²)	Residential (%)	Commercial (%)	Industrial (%)	Agricultural (%)	Open (%)	Rainfall
Berkeley	87.59	57	16	18	0	9	21
Concord							
Concord (220731)	283.96	25	10	7	9	49	17
Concord (220732)	212.54	44	4	1	1	50	21
Concord (220733)	121.72	39	6	7	0	47	21
Concord (220734)	30.05	46	9	26	6	12	17
Fairfield							
Fairfield (220721)	226.20	12	1	5	12	70	25
Fairfield (220722)	131.69	0	0	0	13	86	29
Fairfield (220723/26)	410.25	8	6	2	48	36	21
Fairfield (220724/25)	109.76	0	0	0	1	99	19
Napa River	937.89	10	3	1	24	62	31
Novato	183.98	23	7	1	13	56	33
Petaluma River	377.64	14	1	2	35	48	27
Pinole	152.43	33	5	12	0	49	23
San Francisco Bayside	28.76	58	39	2	0	1	21
San Rafael	157.66	50	8	1	0	41	39
Sonoma Creek	429.77	8	1	1	36	54	29

Table 3-8
Land use specific runoff coefficient and mean selenium concentrations

	Residential	Commercial	Industrial	Agricultural	Open	Source
Runoff coefficient (best estimate)	0.35	0.9	0.9	0.1	0.25	Davis et al. (2000)
Selenium concentration (low end) $\mu\text{g l}^{-1}$	0.36	0.58	0.58	0.50	0.50	BASMAA (1996)
Selenium concentration (high end) $\mu\text{g l}^{-1}$	1.55	1.55	1.55	0.85	0.85	SWAMP

Table 3-9
Estimated total selenium loadings (kg/yr) by land use from hydrological areas draining NSFB by land uses

Hydrological area	Residential	Commercial	Industrial	Agricultural	Open	Total (kg/yr)
Berkeley	14.4	10.4	11.7	0.0	0.9	37.5
Concord	60.7	30.5	24.6	1.1	31.6	148.5
Fairfield	18.8	20.3	16.1	11.5	67.0	133.8
Napa River	40.1	30.9	10.3	15.1	97.3	193.6
Novato	19.2	15.1	2.2	1.7	18.4	56.5
Petaluma River	19.7	3.6	7.2	7.7	26.4	64.6
Pinole	15.9	6.2	14.9	0.0	9.3	46.3
San Francisco Bayside	4.8	8.3	0.4	0.0	0.0	13.6
San Rafael	42.4	17.4	2.2	0.0	13.6	75.6
Sonoma Creek	13.7	4.4	4.4	9.7	36.3	68.6
Total (kg/yr)-SWAMP	249.8	147.2	94.1	46.8	300.8	838.7
Lower bound estimates (kg/yr) - BASMAA	58.4	54.8	35.0	27.7	178.4	354.3
Urban loads ¹ (kg/yr)						491.1 (148.2 lower bound)

¹Urban loads are the sum of residential, commercial, and industrial land uses.

Estimated storm water runoff from urban areas surrounding the NSFB is 316.8 Mm³/yr, about 44% of the total runoff. Estimated loads from urban areas based on the SWAMP concentrations are at 491.1 kg/yr, about 58.6% of loads from all land use types. Because a lower concentration in the agricultural areas compared to other urban land uses was used (0.85 µg/L versus 1.55 µg/L), estimated total selenium loads from all land uses are slightly lower than load estimates in Method 1. Also note for Napa River watershed, because a large portion of the land uses is agricultural, using a lower selenium concentration for agricultural area resulted in lower estimates of selenium loads for the whole hydrological area (193.6 kg/yr versus 281.7 kg/yr in method 1). Estimated loads from urban areas based on the BASMAA concentrations are at 148.2 kg/yr, about 43% of loads from all land use areas.

3.3.5 Tributary Load Summary

Three, somewhat overlapping methods were used to compute tributary loads. Using the SWAMP selenium data from the tributaries, loads were computed using flow from different sources: modeled annual flows from a recent study (Davis et al., 2000) and measured flows from USGS gage stations. The modeled flows were used because of the limited availability of measured flow data. Loads from urban and non-urban areas were also estimated based on modeled runoff and land use specific concentrations derived from BASMAA and SWAMP concentration data. Loads from urban areas generally account for 43% or 59% of total loads from tributaries, depending on the concentrations used.

Driven in large part by relatively high concentrations in the tributaries in both the wet and dry seasons, the average annual loads from the tributaries can be up to 1,511 kg/year depending on the methods used for the load estimation. Much of this load (greater than 95%) is delivered to the bay in the wet months, consistent with the timing of flows, as shown in the calculation using the USGS gage data. The largest single sources of loads are the Napa River, Sonoma Creek, and the Concord hydrological area. Note that selenium is a naturally occurring trace element, and is found even in runoff from open areas. A significant portion of these loadings is associated with natural sources.

On average, the tributary concentration data are generally higher than Sacramento River concentrations, which are more typical of a low background in the region. Although the high average concentrations are not driven by one or two measurements, it is nonetheless clear that the load estimates above are based on a limited amount of data. Furthermore, the SWAMP and BASMAA concentrations differ: lower mean concentrations were observed in BASMAA dataset. However, the range of concentrations (0.06 – 0.90 µg/L after 1/1/1992) indicates that higher concentrations than 0.1 µg/L were not uncommon in local tributaries. Given the underlying data limitations and uncertainty in flows, and the year-to-year variability, estimated loads from tributaries can be as low as 354 kg/yr using BASMAA concentrations and modeled runoff, 834 or 914 kg/yr based on SWAMP concentrations and modeled runoff, and 1511 kg/yr based on SWAMP concentrations and measured flow. For the purpose of this analysis, we go forward with the relatively wide range of 354-834 kg/yr, with about half originating in urban runoff.

Particulate selenium loads from local tributaries were estimated based on previous estimates of total suspended sediment (TSS) loads for different hydrological areas in the Bay Area by Davis et al. (2000). Estimates of TSS loads by Davis et al. (2000) were based on SIMPLE model estimates of runoff multiplied by available TSS concentrations. Data on particulate selenium concentrations are limited from local tributaries. Therefore selenium concentrations in particulates measured for the Sacramento River (0.62 ± 0.21 µg/g; $n=5$) by Doblin et al. (2006) were used in the calculation. TSS loads estimated by Davis et al. (2000) are 1.91×10^8 kg/yr for the North Bay watersheds. With a particulate selenium concentration of 0.62 µg/g, estimated particulate selenium loads from local tributaries are 118.2 kg/yr.

3.4. INPUTS FROM SAN JOAQUIN AND SACRAMENTO RIVERS VIA THE DELTA

Although selenium inputs from the Central Valley via the Delta are expected to be a significant source to the North Bay, accurately estimating these loads is difficult due to the role of the Delta and tidal influences from the bay. Loads upstream of the Delta can be estimated from measurements at Freeport (on the Sacramento River) and at Vernalis (on the San Joaquin River) (Figure 3-7). Inflow originating from the San Joaquin River has high selenium concentrations due to inputs from agricultural drainage (0.68 ± 0.20 µg/L dissolved selenium) and the Sacramento River has much lower selenium concentrations (0.07 ± 0.02 µg/L) (Cutter and Cutter, 2004). However, flows in the San Joaquin River at Vernalis are usually much smaller: 10 to 15 percent of inflow from Sacramento River at Freeport (Figure 3-7). Therefore, on an annual basis loads from both rivers to the Delta are significant. However, selenium processes in the Delta are not well characterized. Besides the normal processes of settling and mixing, a large portion of the water in the Delta is also exported for

agricultural and urban uses in other parts of California. The relative contribution of the Sacramento and San Joaquin Rivers to the overall export from the Delta to the North Bay changes with tidal cycles and season. The contribution from the San Joaquin River can potentially increase during drier months of September to November (Figure 3-7 and Presser and Luoma, 2006). In this section, available flow and concentration data are used to make the best possible estimates of the selenium load contributions of the Delta and the two major rivers to the North Bay.

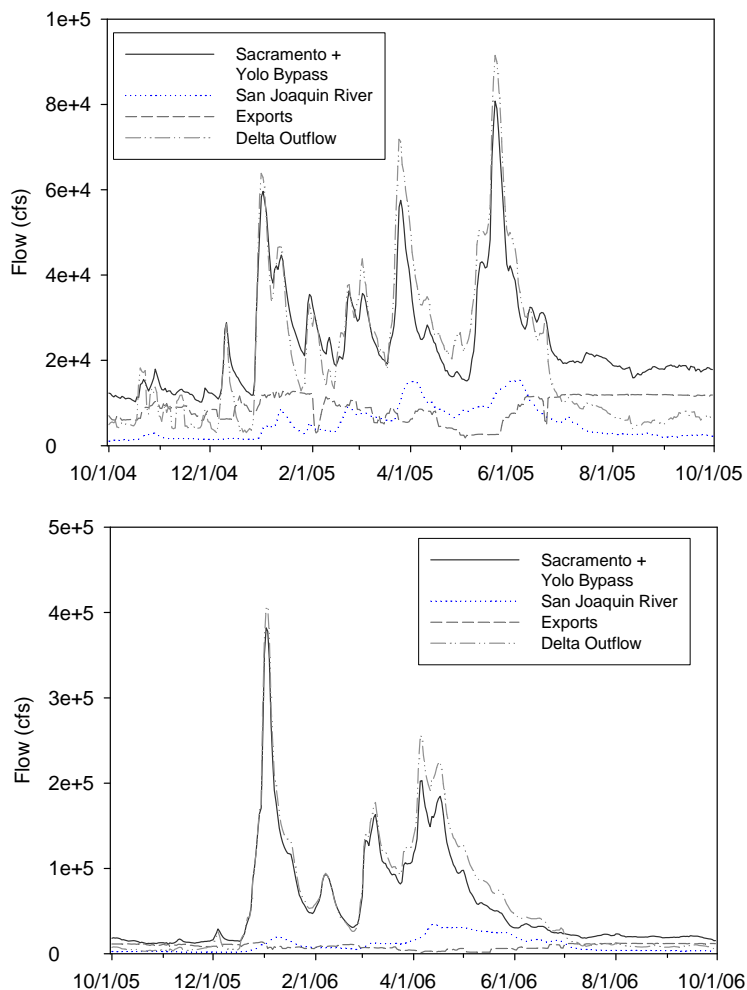


Figure 3-7 Flow from Sacramento River, San Joaquin River, compared to Delta exports (diversions of Central Valley Project, State Water Project, Contra Costa Water District Diversions and North Bay Aqueduct) and outflow to Delta for a dry year (water year 2004) and a wet year (water year 2005) (Data source: IEP).

Selenium data have been collected as part of the RMP just above Mallard Island at the BG20 (Sacramento River) and BG30 (San Joaquin River) stations. Observed total selenium concentrations at these stations (0.15 and 0.18 $\mu\text{g/L}$, respectively) are more representative of Delta concentrations than of the individual rivers. The concentrations are higher than in the Sacramento River at Freeport (0.07 $\mu\text{g/L}$, noted above), and substantially lower than in the San Joaquin River at Vernalis (0.68 $\mu\text{g/L}$), indicating mixing between the two sources, and

possibly tidal influences from the bay during low flow periods. Concentrations observed at BG20 and BG30 also correlate well ($R^2 = 0.59$) possibly due to mixing of common sources. In a separate study, selenium concentrations were found to decrease by 60-80% during transport from the San Joaquin River at Vernalis into the estuary at Antioch (Cutter unpublished data; Meseck and Cutter, 2006).

Different methods have been used in previous studies to calculate riverine inputs of various pollutants through the Delta to the Bay. Davis et al. (2000) used average concentrations at two RMP monitoring stations in the Delta (BG20 and BG30) to estimate loads of different pollutants from Central Valley to the Bay. Leatherbarrow et al. (2005a) and McKee et al. (2006) used continuous monitoring data of SSC at Mallard Island to estimate loads of sediments, mercury and organics to the Bay. With respect to selenium, Presser and Luoma (2006) estimated loads from the two rivers (Sacramento River at Freeport and San Joaquin River at Vernalis) separately to estimate selenium inputs to the Bay. Cutter and Cutter (2004) and Abu-Saba and Ogle (2005) used the approach of flow weighting concentrations from the two rivers to calculate a riverine concentration and multiplied this by the net Delta outflow to estimate loads from the Delta to the bay. Meseck (2002) applied a "Delta removal constant" to the riverine loads to take into account the possible selenium sink in the Delta in her modeling analysis.

Here we used three different approaches to estimate the selenium loadings from Central Valley via Delta to the bay based on the available data. The first approach is the simple approach similar to Davis et al. (2000), which uses average concentration of two RMP stations in the Delta and multiplies it by the net Delta outflow. The second approach uses selenium loadings from the Sacramento and the San Joaquin Rivers separately based on data from Cutter and Cutter (2004) and applies a "Delta removal constant" similar to Meseck (2002) to account for the possible selenium loss in the Delta. The third approach is independent of the prior two, in which the loadings from Central Valley to the bay were estimated as the difference between inputs from the two rivers minus the export through aqueducts. The third method can be used to estimate the relative selenium load contribution of the two rivers to the bay.

3.4.1 Method 1. Loadings Based on the RMP data and Tidally Corrected Delta Outflows

For the first approach, tidally corrected outflow data from the Delta were obtained from the Interagency Ecological Program (IEP) (<http://www.iep.ca.gov/dayflow/index.html>). Outflows from the Delta show large year-to-year variations (Figure 3-8). Concentrations measured at BG20 and BG30 also show year-to-year variations, and no correlation with the Delta outflow and no clear pattern in wet versus dry seasons were observed.

Daily selenium loadings were estimated by multiplying daily Delta outflow with the average concentrations at BG20 and BG30 of the dry and wet seasons of each year. The estimated daily loadings were summed to compute annual loadings. Estimated annual loadings are highly variable (by a factor of 12) depending on the volume of outflow from the Delta (Table 3-10 and Figure 3-9). Water year 1998 was an exceptionally wet year. Excluding 1998, estimated annual loadings vary by a factor 6 among the years. Loadings from the Delta are more significant in the wet season than the dry season (Figure 3-9). An average load of 3,962 kg/year from the Delta to the North Bay was estimated (1994-2006).

There is some limited evidence that the Delta load may be higher than computed using this method and using BG-20 and BG-30 concentrations from the RMP. Selenium concentrations have been measured in the outflow from the Delta (Mallard Island) during the storm events of 2005 - 2006 ($0.46 \pm 0.13 \mu\text{g/L}$; L. McKee, personal communication), and separate from the RMP data. Higher concentrations observed at Mallard Island during storm events suggest potential of higher loadings during these periods. Total recoverable selenium concentrations during storm events are a function of daily flow, suggesting a dilution behavior (Figure 3-10). Nonetheless, the relationship was used to estimate total selenium loadings during high flow. The result indicates a potential of 16-56% underestimate of total selenium loadings using BG20 and BG30 concentrations (e.g. 1,059 kg/yr vs. 1,590 kg/yr for a dry year 2001 and 5,078 kg/yr vs. 21,000 kg/yr for wet year 2006). However, the storm selenium concentration data are very limited at this point, and the more complete RMP data record is recommended for calculation of long term Delta loads.

Leatherbarrow et al. (2005a) used concentrations measured at Mallard Island to estimate loads of PCB (polychlorinated biphenyls), PAH (polycyclic aromatic hydrocarbons), OC (Organochlorine) pesticides, and Hg from the Delta to the Bay. Contaminant loads were estimated based on relationships between contaminants and SSC, and the estimated sediment loads using available flow information and continuous SSC concentrations measured at Mallard Island. In quantifying loads of sediment from Mallard Island to the Bay, both the advective and dispersive loads were estimated. The relative contributions of the advective and dispersive load were estimated using point velocity and concentration measured during water year 1994 and 1996 (McKee et al. 2006). During a wet period (mean discharge = $2116 \text{ m}^3/\text{s}$), dispersive point-load averages about 11% of the advective point load. Due to the tidal influence at Mallard Island, dispersive loads (most commonly landward) can be a significant portion of total load during low flow period. Estimated dispersive load for a low flow period (April 15, 1994-June 4, 1994) was 49% of advective point load at surface and 52% at mid-depth (McKee et al. 2006). Overall the dispersive loads of sediment were estimated to be 0.24 Mt/yr or 20% of the total loads for the 9 year period of 1995-2003. There is limited applicability of this method for total selenium loadings because most selenium (at least two-thirds, and often more) is in the dissolved form. However, the sediment load estimates are used to estimate particulate loads of selenium from the Delta to the bay. The calculation appears at the end of this section.

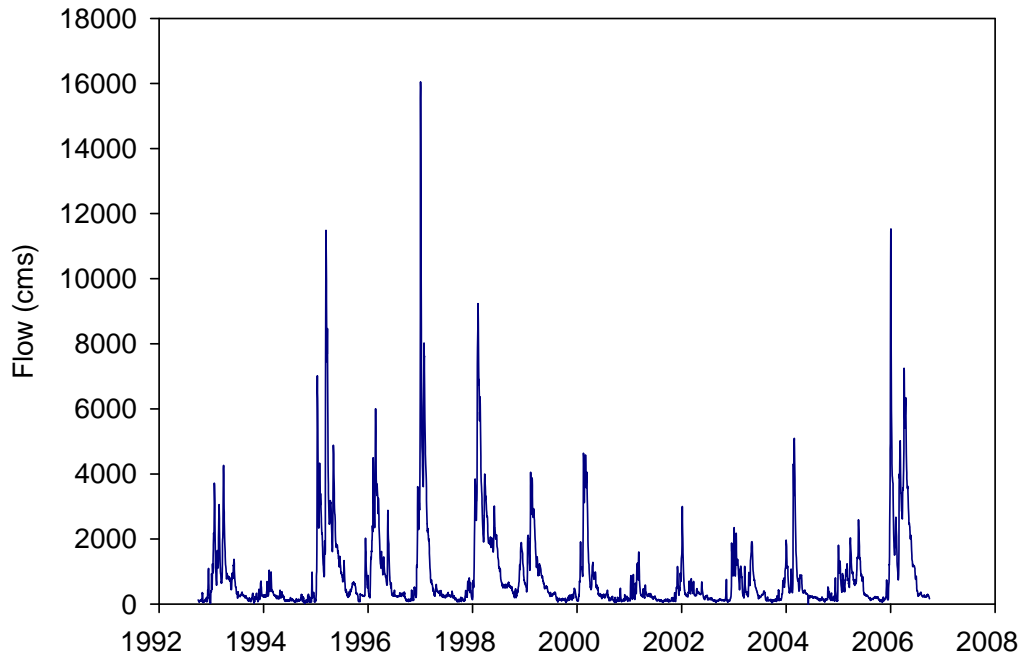


Figure 3-8 Daily Delta outflow for water years 1992-2006 (Data source: IEP)

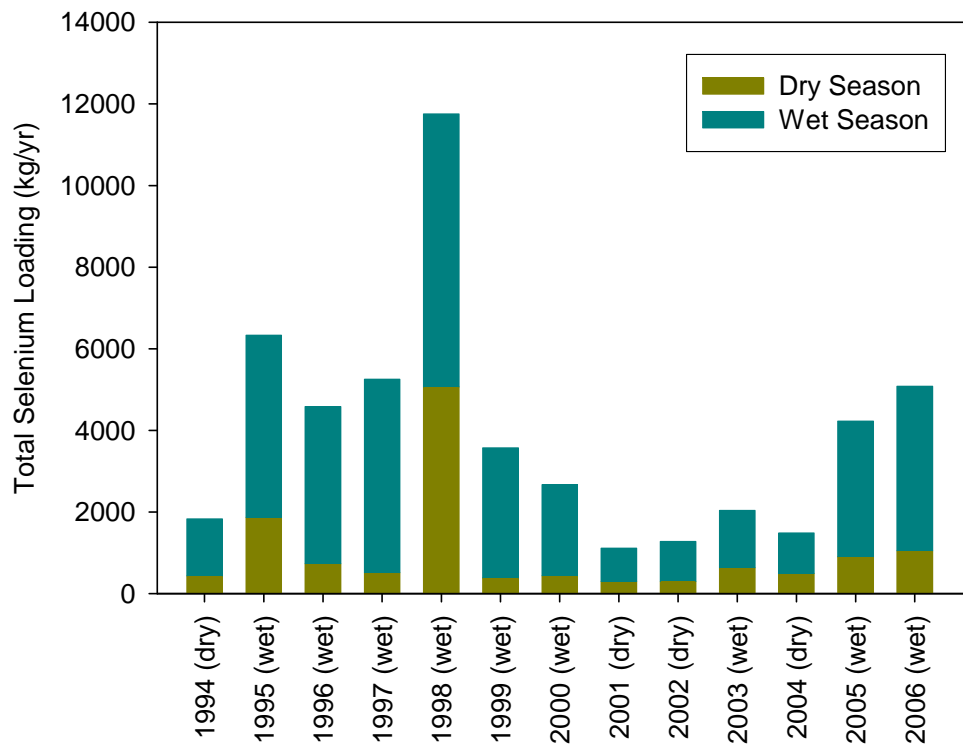


Figure 3-9 Estimated wet and dry season total selenium loadings from Delta to the Bay by water year.

Table 3-10
Estimated total and dissolved selenium loadings from the Delta

Year	Delta outflow m ³	Loadings (total) kg/yr	Loadings (dissolved) kg/yr
1994	7.42E+09	1,831	1,647
1995	4.11E+10	6,859	6,159
1996	2.56E+10	4,355	2,818
1997	4.23E+10	5,252	4,399
1998	5.36E+10	11,752	9,736
1999	2.78E+10	3,572	3,292
2000	2.24E+10	2,666	1,495
2001	8.56E+09	1,110	882
2002	1.13E+10	1,276	814
2003	1.73E+10	2,037	1,797
2004	1.84E+10	1,485	2,259
2005	1.90E+10	4,228	4,337
2006	5.40E+10	5,078	3,970
Average	2.68E+10	3,962	3,354

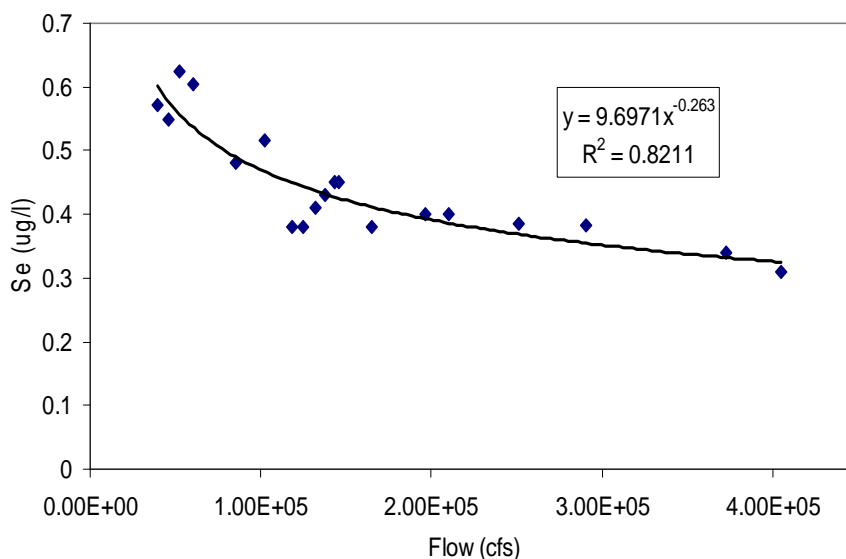


Figure 3-10 Relationship between total selenium concentrations and flow at Mallard Island (Data source: L. McKee).

3.4.2 Method 2: Loadings Based on Riverine Loads to the Delta, and Assumption of Delta Removal Constant

Dissolved selenium concentrations in the Sacramento River at Freeport sampled by Cutter and Cutter (2004) on biweekly or monthly basis indicated relatively small changes from 1984 to 2000 (Figure 3-11). Dissolved selenium concentrations in the Sacramento River (at

Freeport) range between 0.01-0.13 $\mu\text{g/L}$, with an average of $0.07 \pm 0.02 \mu\text{g/L}$ for the period of 1999-2000. Dissolved selenium concentrations in the San Joaquin River at Vernalis may be 10 times higher. Concentrations for the San Joaquin River at Vernalis range between 0.14 - 4.69 $\mu\text{g/L}$ for entire period of record. A significant decrease in selenium concentrations was observed for 1999-2000 compared to the 1980s sampling. Mean dissolved selenium concentration for the period of 1999-2000 is $0.68 \pm 0.20 \mu\text{g/L}$.

Concentrations during 1999-2000 show some variations both in the Sacramento and San Joaquin River (Figure 3-12). For the Sacramento River, higher concentrations were observed for the months between April to July. For the San Joaquin River, no clear seasonal pattern was observed. Concentrations in relation to flow are shown in Figure 3-13. For the Sacramento River, no clear relationship between flow and concentrations was observed for the recent years, consistent with findings in Cutter and Cutter (2004). Cutter and Cutter (2004) reported a poor correlation between river discharge and any dissolved selenium forms for the Sacramento River. For San Joaquin River, a negative relationship between concentrations and flow was observed, possibly due to the dilution of selenium discharge by natural flow.

For the Sacramento River, due to the weak relationship between dissolved selenium concentration and flow, monthly concentrations were used to calculate the daily loadings. For the San Joaquin River, the flow and concentration relationship derived was used to estimate daily concentrations based on flow. The daily loading was then estimated based on daily flow and estimated daily concentration. Daily flow for the Sacramento River at Freeport (USGS 11447650) and the San Joaquin River at Vernalis (USGS 11302500) were obtained from the USGS website (http://waterdata.usgs.gov/nwis/dv/?refered_module=sw). The estimated daily loadings were summed to calculate the seasonal loadings. The wet season was defined as Oct 1st to Apr. 30th and the dry season was defined as May 1st to Sep 30th (Tetra Tech, 2006).

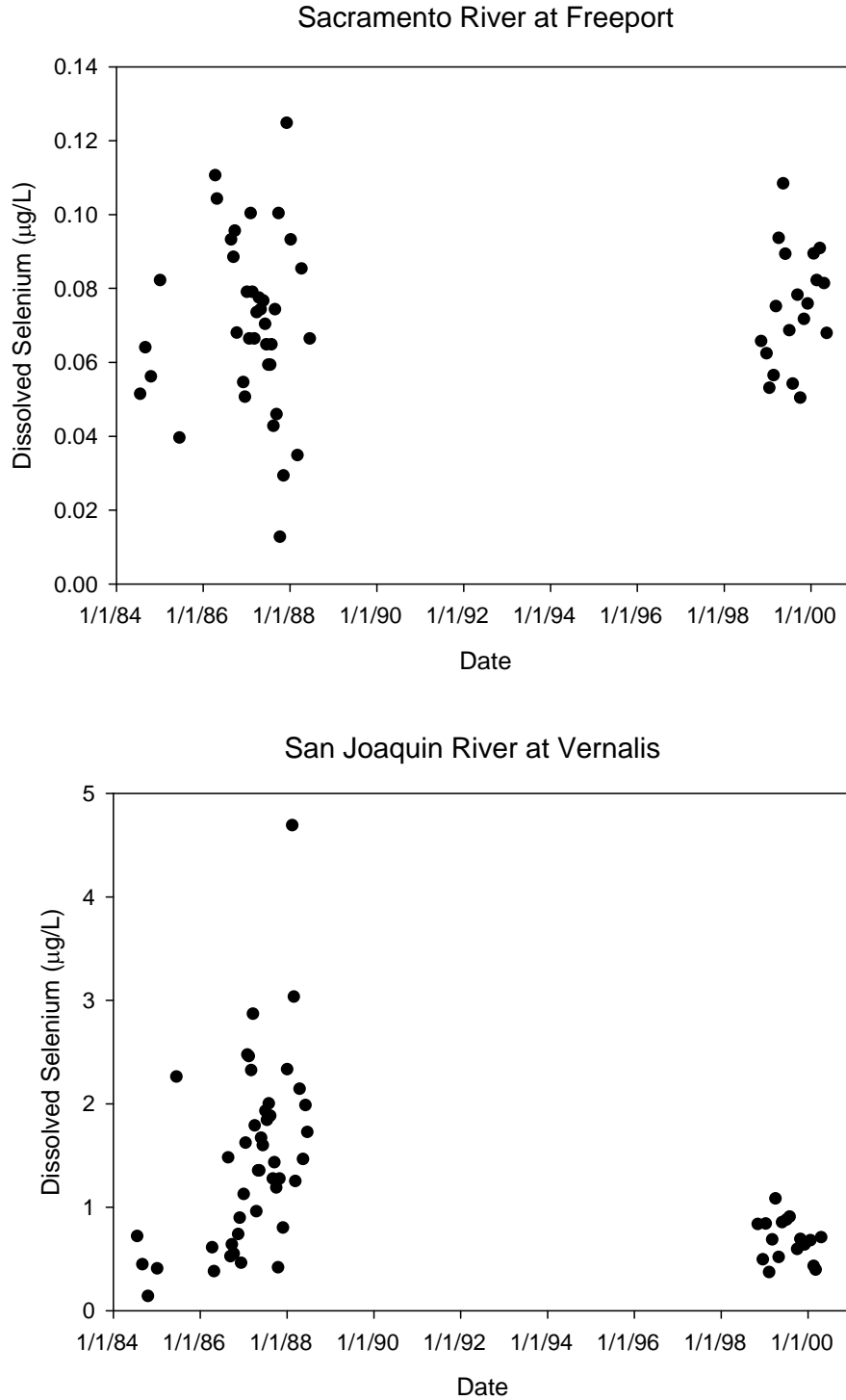


Figure 3-11 Dissolved selenium concentrations in Sacramento River at Freeport and San Joaquin River at Vernalis during 1984-1988 and 1998-2000, sampled by Cutter and Cutter (2004).

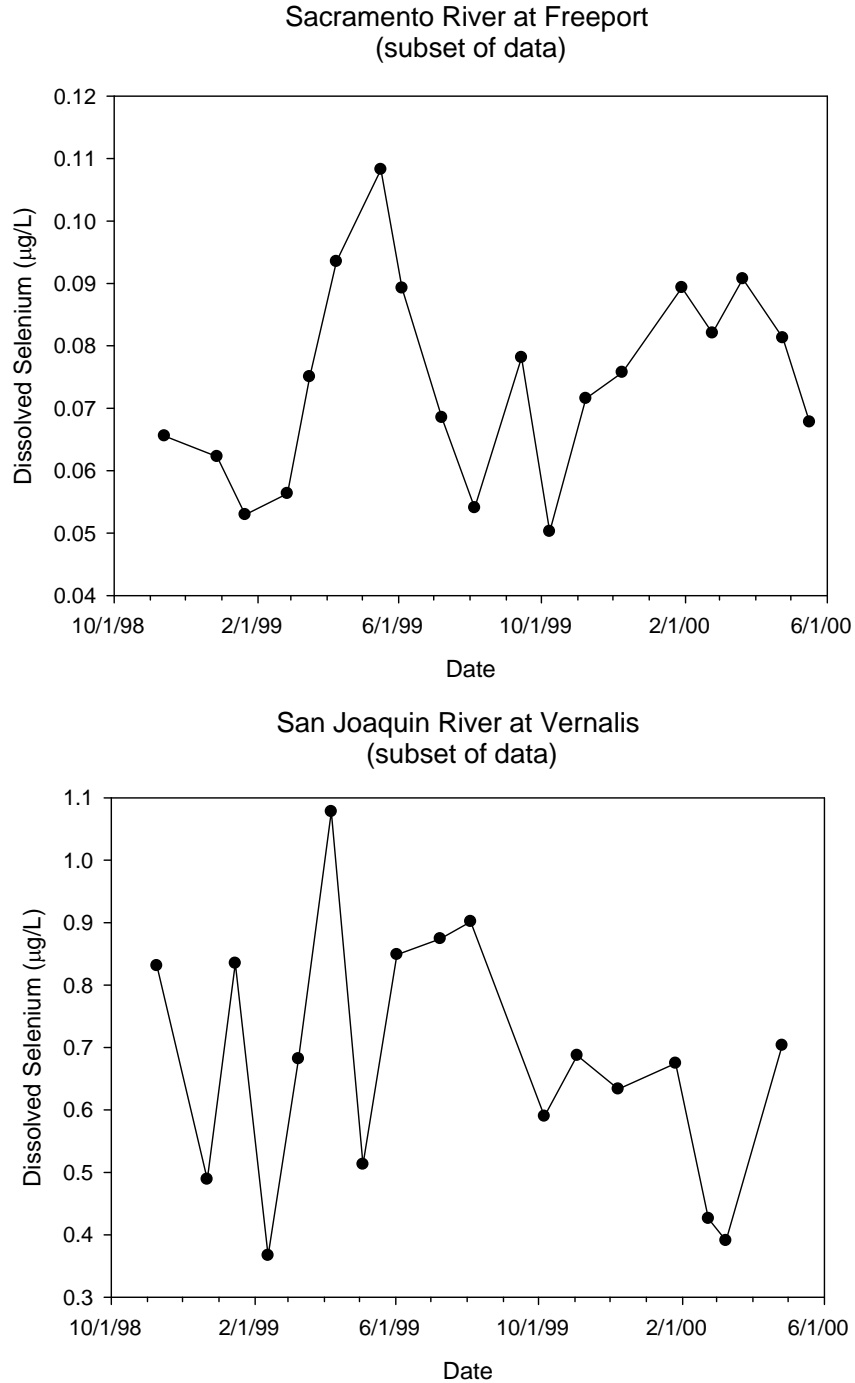


Figure 3-12 Dissolved selenium concentrations at Sacramento River at Freeport and San Joaquin River at Vernalis during 1998-2000, sampled by Cutter and Cutter (2004).

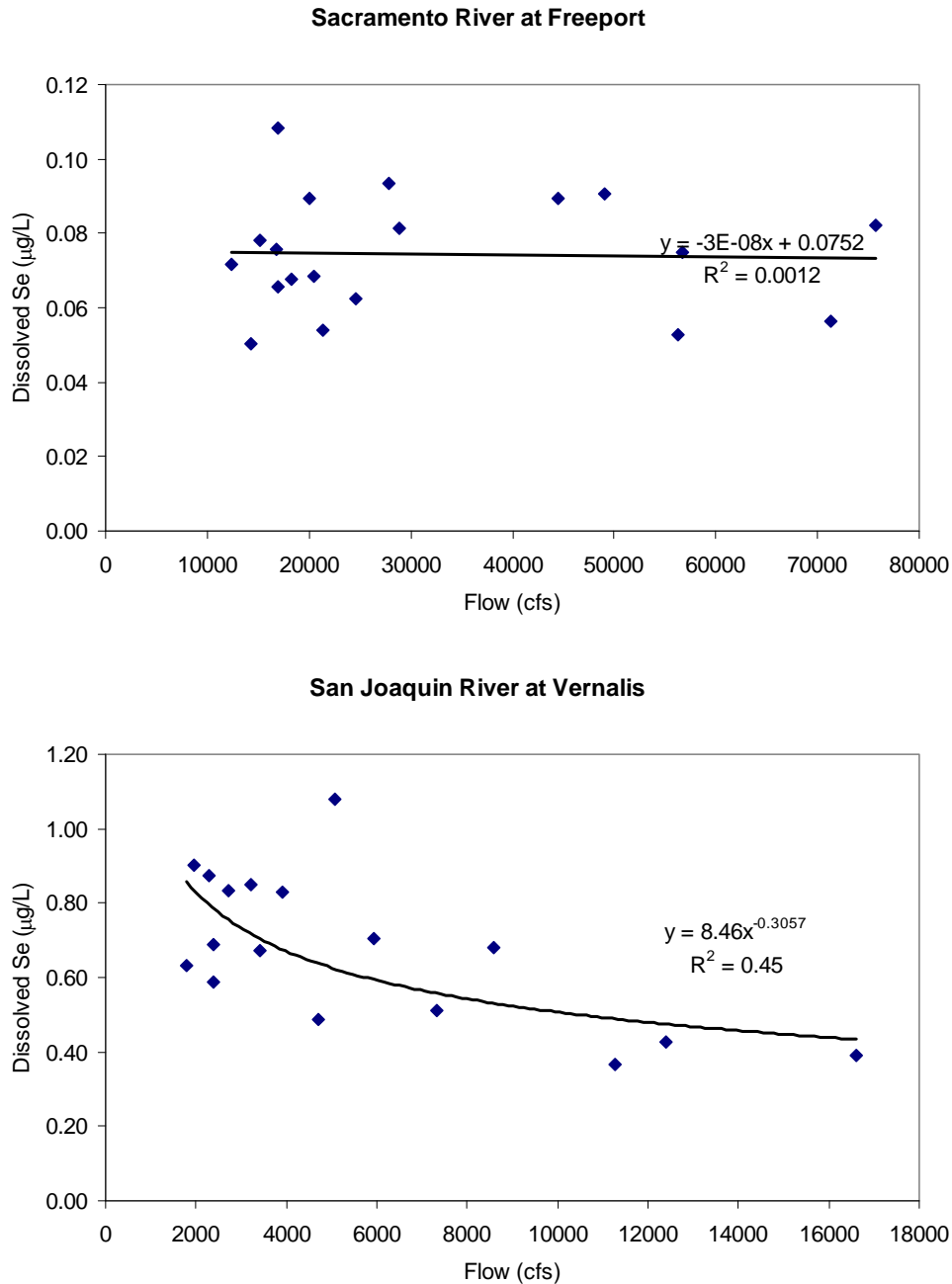


Figure 3-13 Relationship between dissolved selenium concentrations and daily flow for Sacramento River at Freeport and San Joaquin River at Vernalis for the period of 1998-2000 (data source: Cutter and Cutter, 2004). Note that dissolved selenium concentrations show no correlation with flow rate for the Sacramento River.

The estimated annual dissolved selenium loadings range between 703 – 2,693 kg/yr for the Sacramento River at Freeport and 867 – 4,710 kg/ yr for the San Joaquin River at Vernalis. Estimated dry season loadings range between 234 – 1,074 kg/yr for the Sacramento River (at Freeport) and 261-2,097 kg/yr for the San Joaquin River (at Vernalis). Estimated wet season loadings range between 417- 1,748 kg/yr for Sacramento River and 552- 3,048 kg/yr for San

Joaquin River. On average, dry season loadings are generally lower and represent 58% and 60% of the wet season loadings for the Sacramento River (at Freeport) and the San Joaquin River (at Vernalis), with only one exception (San Joaquin River in 1995).

Estimated annual dissolved selenium loadings vary with water years (Figure 3-14). Annual loadings can be as high as 2,600-2,700 kg/yr during wet years for the Sacramento River (at Freeport) and approximately 750 – 1,000 kg/yr during dry years. Annual loadings for the San Joaquin River (at Vernalis) also vary with hydrological conditions. Annual loadings can be greater than 4,000 kg/yr during wet years and less than 1,000 kg/yr during dry years. Overall, average dissolved selenium loadings are higher for the San Joaquin River (at Vernalis) than the Sacramento River (at Freeport) (2,380 kg/yr vs. 1,634 kg/yr during 1990-2007).

Total selenium concentrations were also measured by the SWAMP program at San Joaquin River at Vernalis (Airport Way) on a weekly basis by Central Valley Water Quality Control Board (http://www.waterboards.ca.gov/centralvalley/water_issues/water_quality_studies/surface_water_ambient_monitoring/). The observed total selenium concentrations were higher during the 1980s and early 1990s compared to recent years (Figure 3-15). Dissolved selenium concentrations for the same period measured by Cutter and Cutter (2004) agree relatively well with the total selenium concentrations observed in the SWAMP study but were slightly lower (Figure 3-16). This is to be expected as dissolved selenium usually accounts for 80-95% of total selenium measured. The observed decreases of selenium concentration at Vernalis most likely resulted from the implementation of the Grassland Bypass Project in 1996, which has led to a 60% decrease in selenium loads from the Grassland Drainage Area from pre-project conditions (www.sfei.org/grassland/reports/). However, the magnitudes of the decrease were more significant just below the Grassland Bypass Project area (at Crow's Landing). With transport downstream, the change in concentration was smaller, likely due to inflow from other tributaries (Figure 3-17). Concentrations are generally lower during the wet years (1996 and 2006) and a negative correlation between flow and concentrations was noted (Figure 3-18). The weekly total selenium concentrations measured by SWAMP were extrapolated to daily concentrations for the week and multiplied by daily flow to estimate daily total selenium loadings for the San Joaquin River. Estimated daily loadings were summed up to calculate seasonal and annual loadings (Figure 3-19). Estimated annual loadings for total selenium based on SWAMP dataset are generally comparable to although slightly higher than loadings of dissolved selenium estimated from the Cutter and Cutter (2004) data (Figure 3-20) except for water years 1998 and 2006, when larger discrepancies between the two methods were observed.

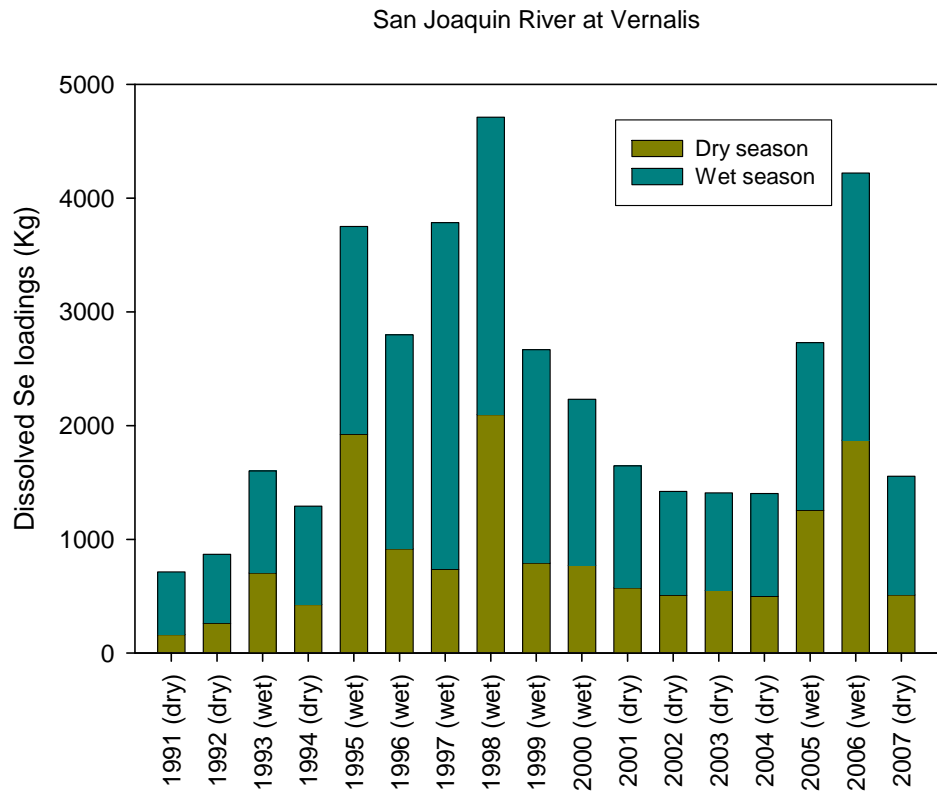
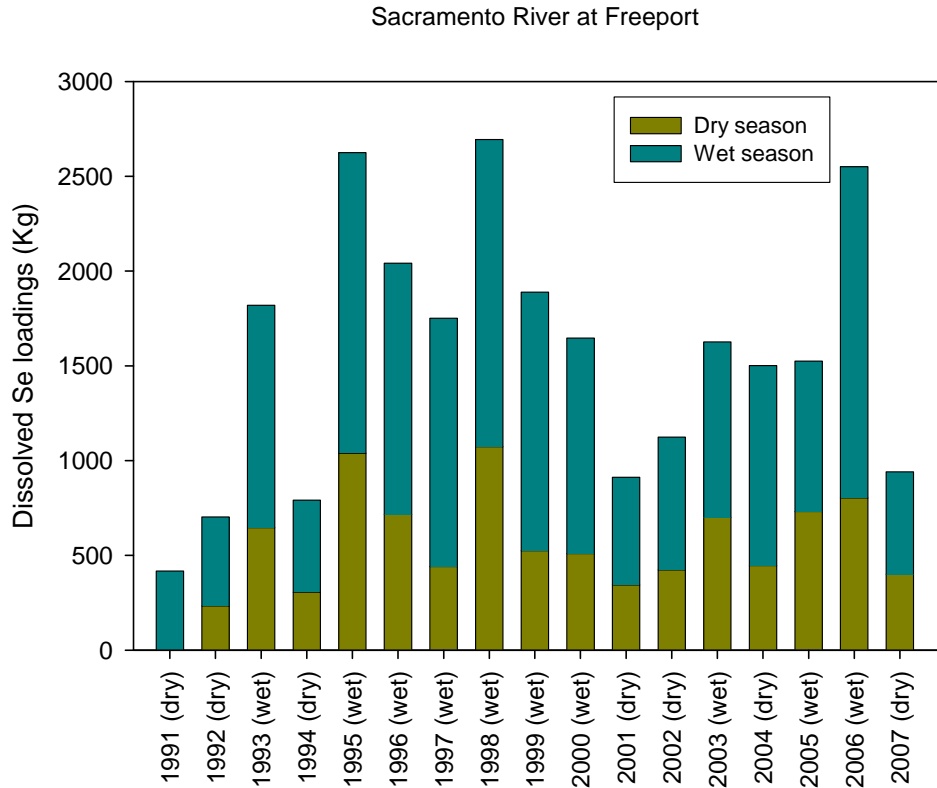


Figure 3-14 Dry and wet season dissolved selenium loadings at Sacramento River at Freeport and San Joaquin River at Vernalis for 1991-2007.

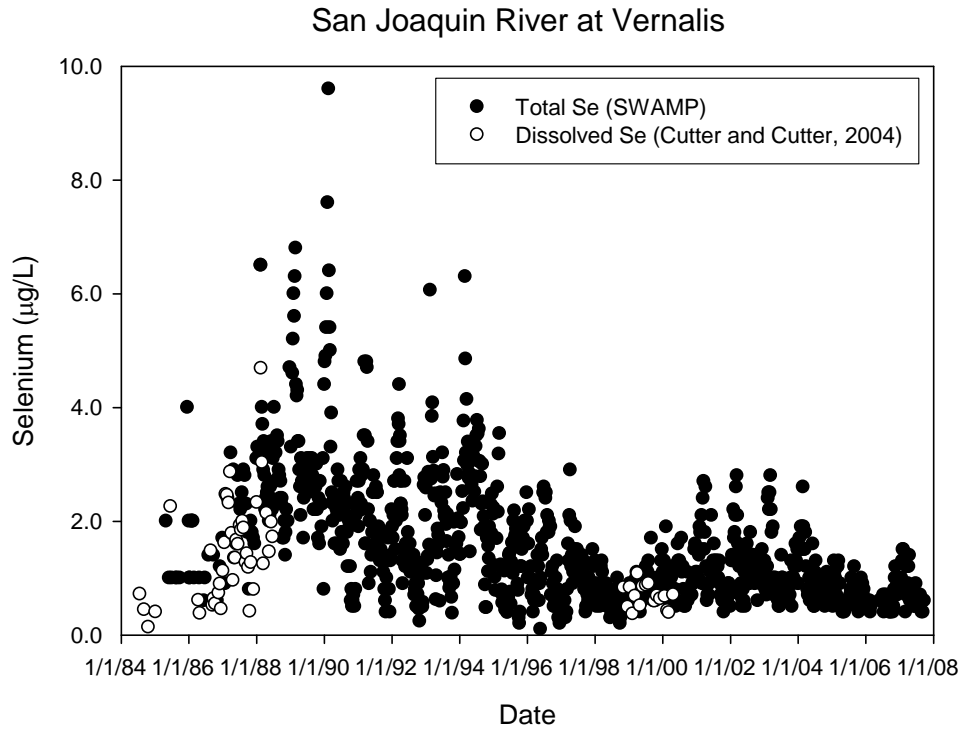


Figure 3-15 Dissolved selenium concentrations sampled by Cutter and Cutter (2004) at San Joaquin River at Vernalis compared to total selenium concentrations observed in SWAMP study.

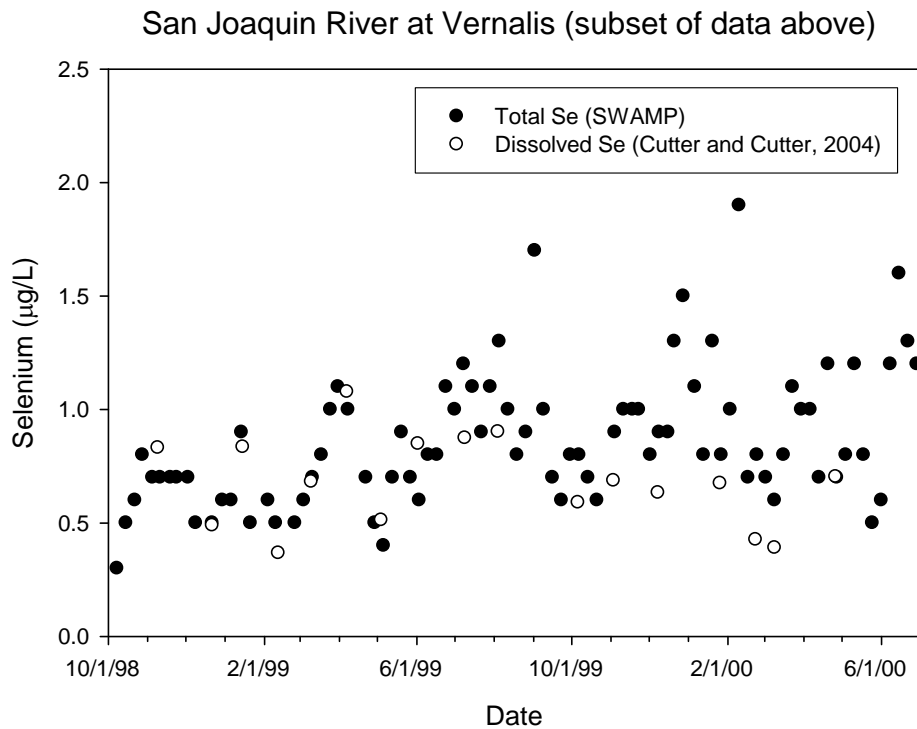


Figure 3-16 A subset of dissolved selenium concentrations sampled by Cutter and Cutter (2004) compared to total selenium concentrations from SWAMP.

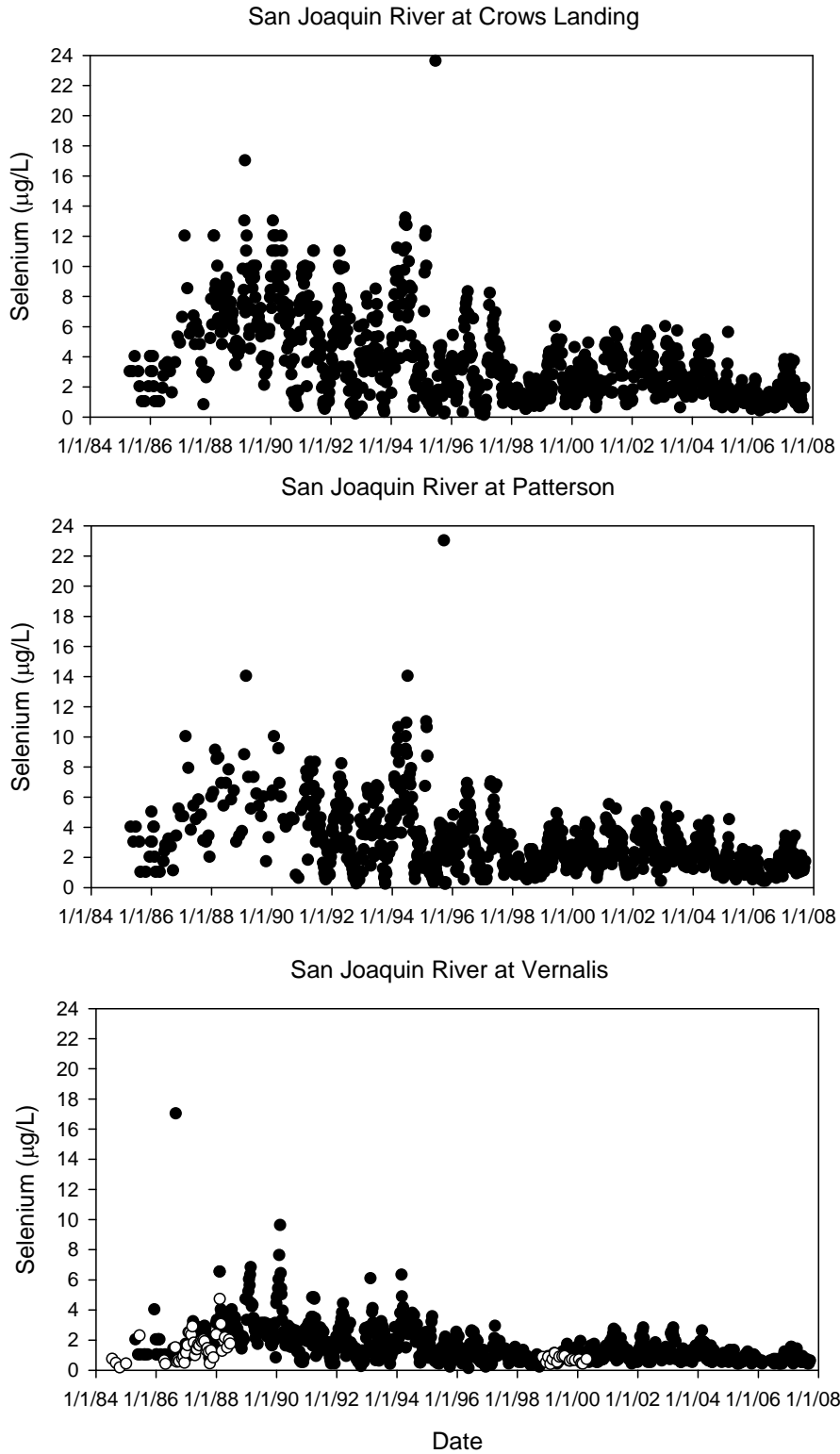


Figure 3-17 Total selenium concentrations along main stem of San Joaquin River at Crows Landing (below grassland bypass project), at Patterson, and at Vernalis (Data Source: Central Valley RWQCB)

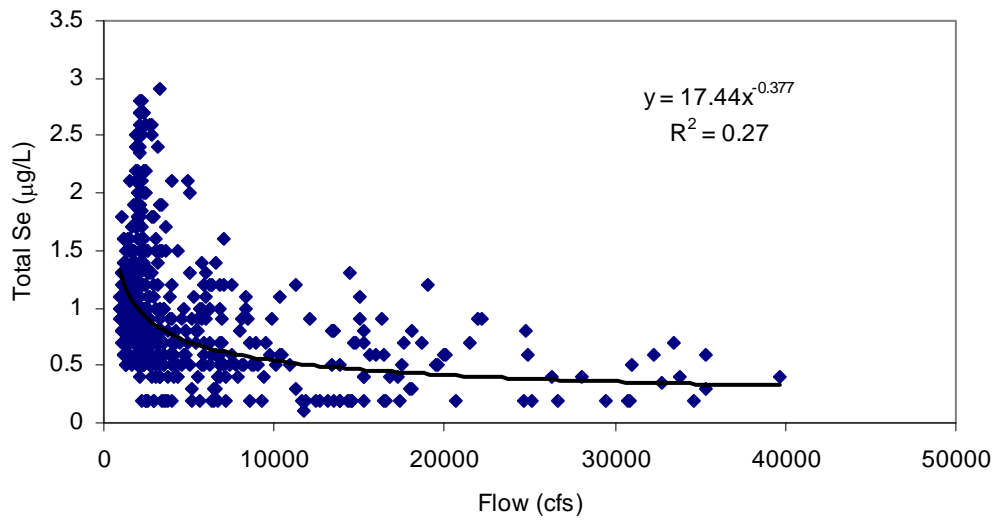


Figure 3-18 Relationship between total selenium and flow at San Joaquin River at Vernalis (Data source: Central Valley Regional Water Quality Control Board SWAMP study and USGS).

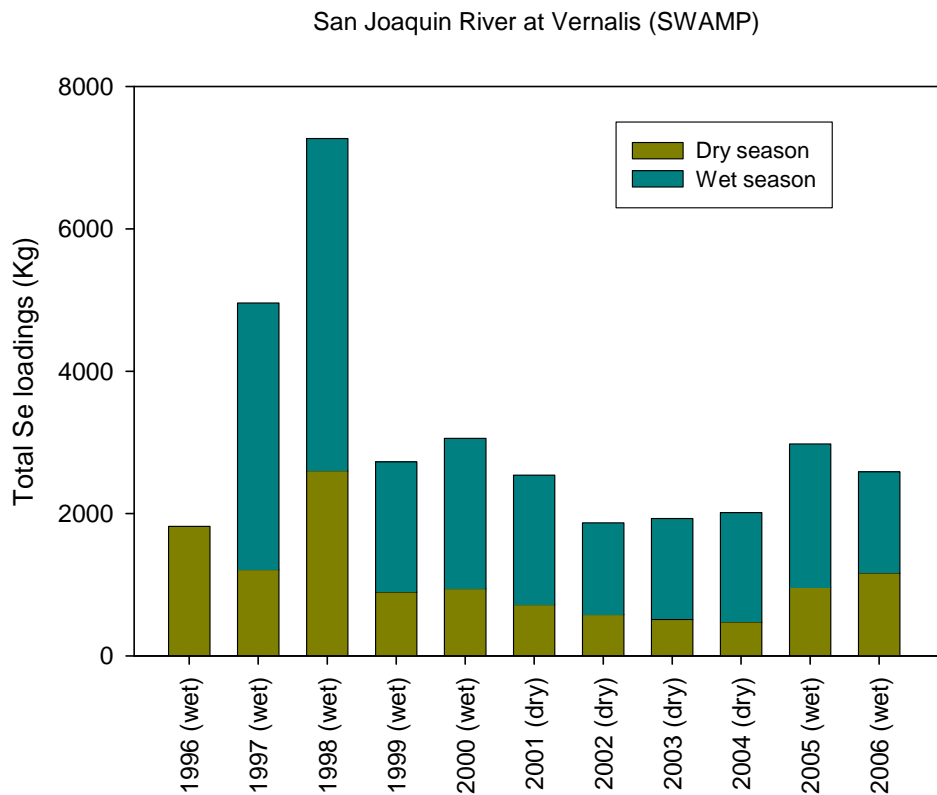


Figure 3-19 Dry and wet season total selenium loadings at San Joaquin River at Vernalis, estimated from concentrations from SWAMP study.

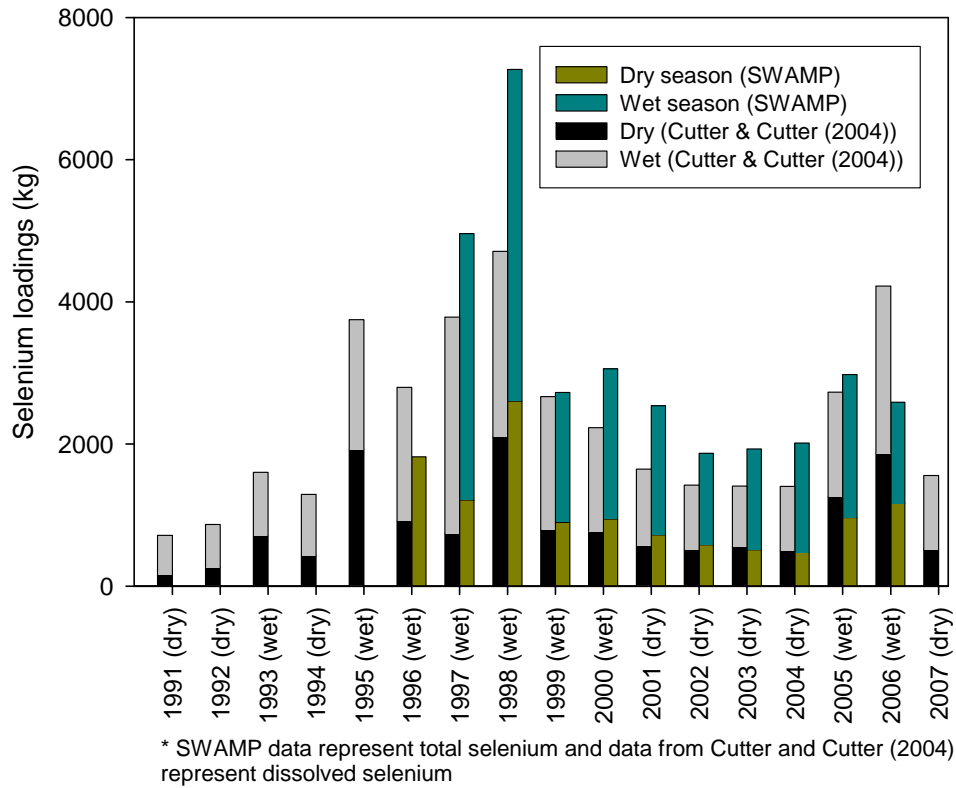


Figure 3-20 Comparison of selenium loadings at San Joaquin River at Vernalis estimated from Cutter and Cutter (2004) data and data from SWAMP study.

Biogeochemical processes in the Delta could potentially serve as a mechanism to remove high selenium concentrations originated from the San Joaquin River. As shown in Figure 3-21, during two low flow sampling events, dissolved selenium concentrations were high in close proximity to the San Joaquin River and decrease through the Delta. Dissolved selenium concentrations at the head of estuary were much lower than the concentrations observed close to the river.

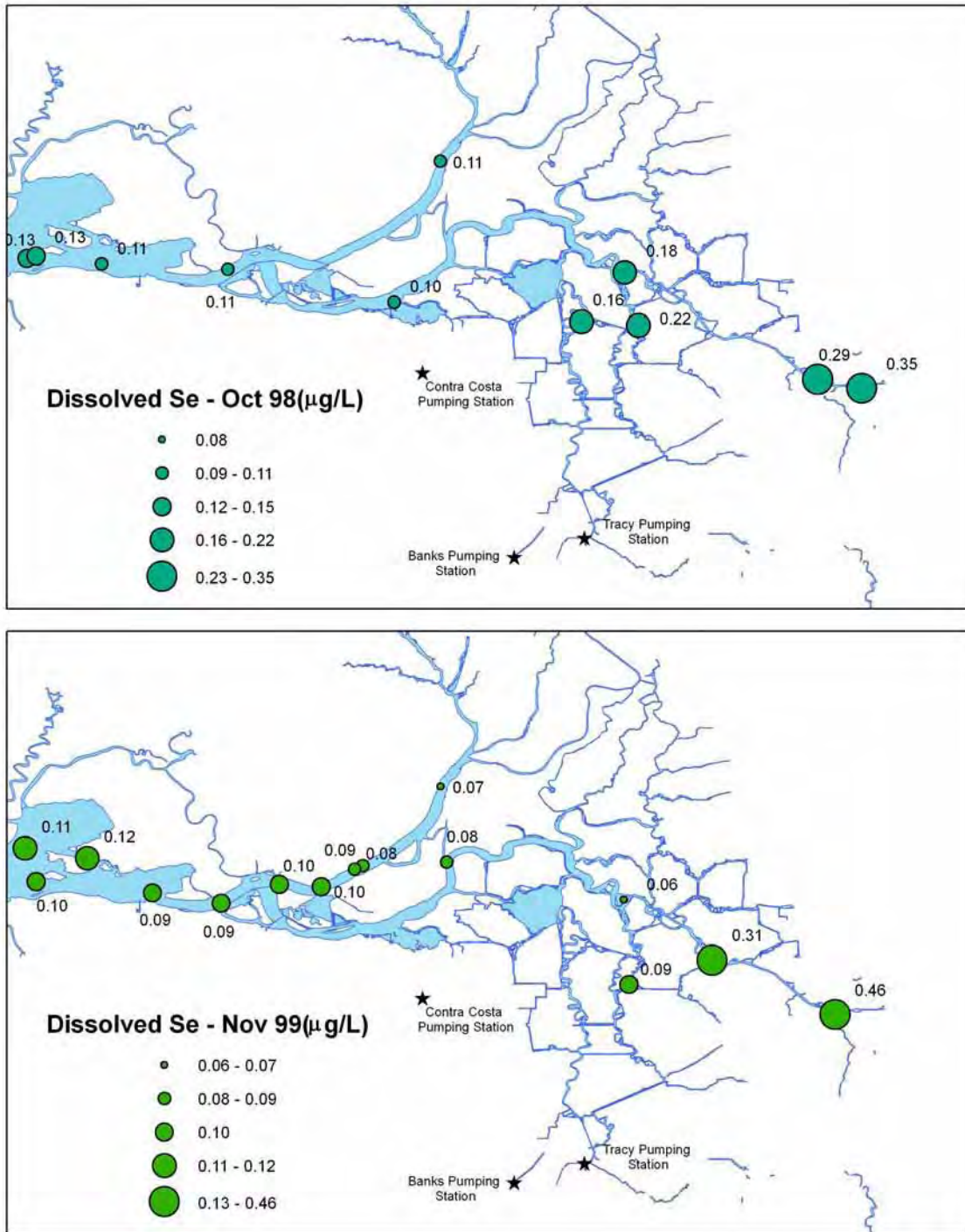


Figure 3-21 Dissolved selenium concentrations at various locations of the Delta and North Bay in October 1998 (NDOI = 4.27×10^{10} L/d) and November 1999 (NDOI = 1.07×10^{10} L/d) sampling (Cutter and Cutter, 2004).

Meseck (2002) fitted sine wave equations to selenium data from the Sacramento and San Joaquin Rivers, and used the fitted functions to estimate riverine loads. Based on samples collected during fall 1998 and summer 2000, selenium concentrations at Vernalis are reduced by 60-80% after being transported through Delta into the estuary at Antioch.

Therefore, Meseck (2002) applied a “Delta removal” constant of 60% to predict actual input of selenium at Antioch from the San Joaquin River.

Using the approach described by Meseck (2002), if a removal constant of 60% was applied to the San Joaquin River inputs, resulting dissolved selenium loading based on estimated river loadings varies between 1,005- 4,578 kg/yr (Figure 3-22). The estimated loadings were compared to Method 1, above, for each year. The percent absolute difference between the two methods for each individual year ranges between 6.3-51.9% except for 1998, an unusually wet year. For 1998, previous method estimated a significantly higher loading of 9,736 kg/yr compared to 4,578 kg/yr using the second approach.

For this method, an average load of 2,493 kg/yr for 1991-2007 from Delta to the Bay was estimated. Average load at Sacramento River at Freeport is 1,577 kg/yr. Average load at San Joaquin River at Vernalis is 2,289 kg/yr.

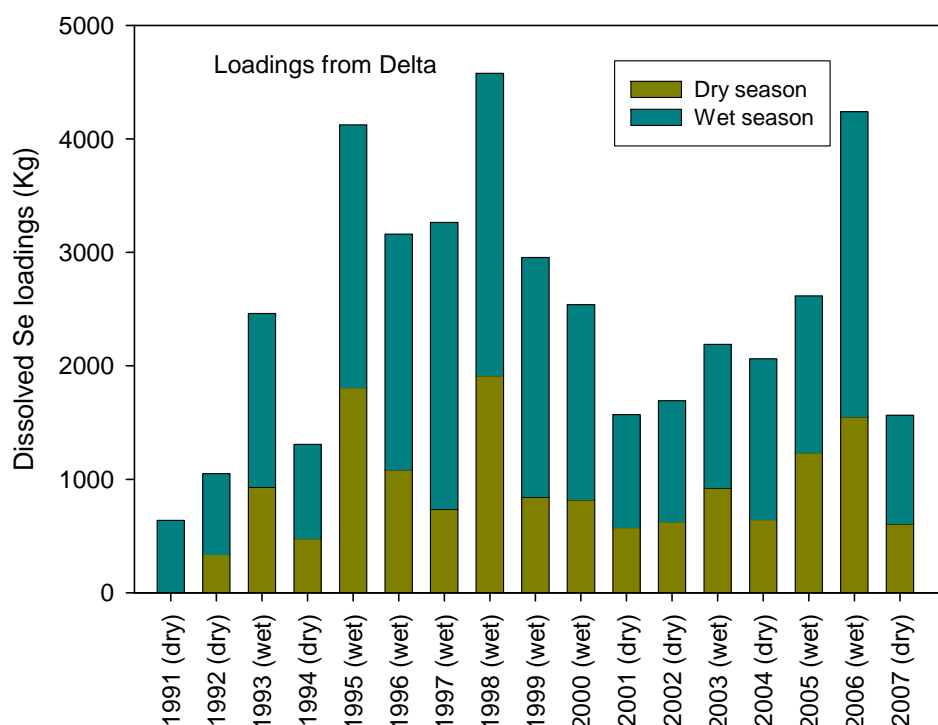


Figure 3-22 Estimated selenium loadings from the Delta to the bay as a result of inputs from Sacramento River at Freeport and San Joaquin River at Vernalis, assuming a “Delta Removal Constant” of 0.60.

Both Methods 1 and 2 have limitations in estimating selenium loads from the Delta. The previous method based on RMP monitoring data set at BG20 and BG30, has the potential issue of overestimating loads during dry season due to tidal influence. The second method, through applying a “Delta removal constant” cannot account for the varying impacts of Delta on the selenium inputs to the Bay. As discussed next, an alternative is to consider outflow data from the Delta through aqueducts, and the estimated selenium concentrations in these outflows, to evaluate the net loads delivered to bay.

3.4.3 Method 3. Calculate selenium loadings to bay by accounting for export through aqueducts

Average export of water from Delta through aqueducts was $6.82 \pm 0.90 \times 10^9$ m³/yr during 1994-2006. Flow at pumping plants is mostly dominated by Sacramento River water. During some periods, San Joaquin River water can also dominate. Assuming equal volume mixing of the two rivers, the selenium concentration in pumping plants is approximately 0.4 µg/L (0.07 µg/L at Sacramento River at Freeport and 0.68 µg/L at San Joaquin River at Vernalis). Assuming a concentration range of 0.1 µg/L (low end, when Sacramento River dominates) to 0.4 µg/L, the export of selenium through aqueducts is likely to range between 700- 2,700 kg/yr. For critically dry years during 1986-1998, Presser and Luoma (2006) estimated an aqueduct export of 1,557 kg/6 months, a value comparable to the higher end of this estimated range.

A more detailed computation of the riverine contribution to exports can also be performed. The contribution of the Sacramento and San Joaquin Rivers or other relatively minor inflows to State Water Project (SWP) pumping plant at Banks was previously modeled using a hydrodynamic model (Delta Simulation Model, Version 2, or DSM2) by the California Department of Water Resources (DWR). Results from DSM2 simulations indicated that during dry years or in the dry season, Sacramento River is the major source of flow at Banks pumping plant (DWR 2004; Figure 3-23). During wet years or in wet seasons, San Joaquin River can contribute a large portion of the flow. Results from these DSM2 fingerprinting simulations were used to estimate selenium concentrations at the pumping plant based on concentrations from the Sacramento and San Joaquin Rivers, and selenium loads exported through aqueducts.

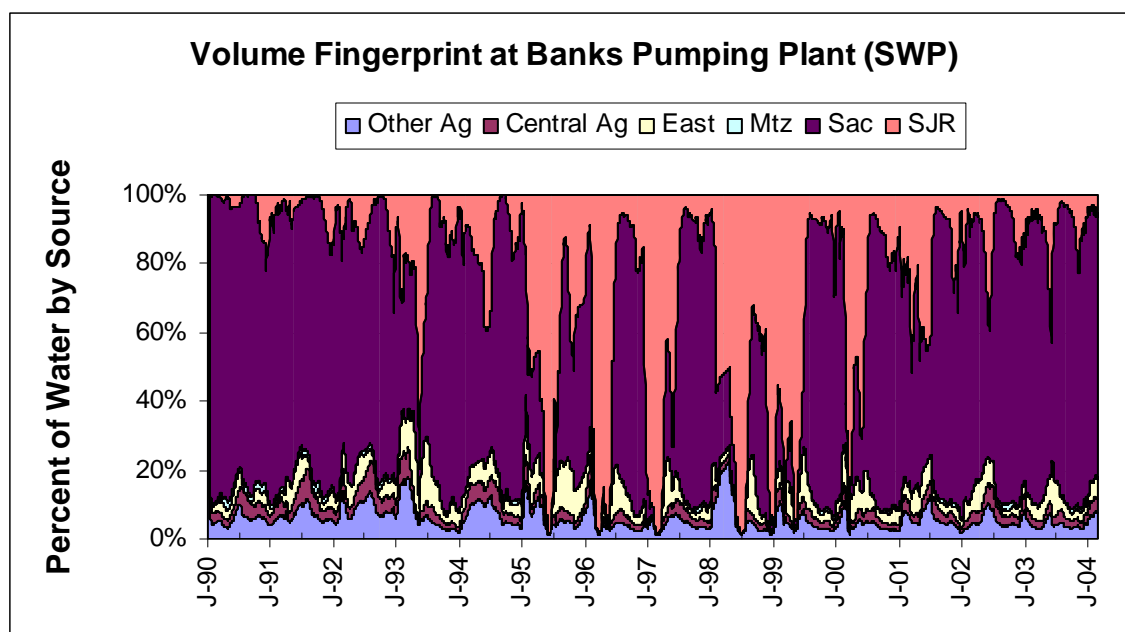


Figure 3-23 Long-term percentage contribution of flows at the Banks Pumping Plant (data provided by DWR; Tetra Tech, 2006).

Concentrations at pumping plants were estimated as:

$$C_{exp} = (Q_{sac} * C_{sac} + Q_{sjr} * C_{sjr}) / Q_{exp} \quad (1)$$

Where C_{exp} is daily concentration in the aqueduct, Q_{sac} is export flow originating from the Sacramento River, C_{sac} is daily selenium concentration at the Sacramento River at Freeport (estimated from monthly concentrations from Cutter and Cutter, 2004), Q_{sjr} is export flow originating from the San Joaquin River, C_{sjr} is daily selenium concentration at the San Joaquin River (estimated previously based on relationship between flow and concentrations using data from Cutter and Cutter, 2004), and Q_{exp} is total flow through the aqueducts (includes the Central Valley Project, State Water Project, Contra Costa Water District, and North Bay Aqueduct). We made the assumption that the flow composition from the two rivers at Banks pumping plant is the same as the other pumping plants.

Estimated concentrations in the aqueduct were multiplied by the export flow (obtained from DAYFLOW) to calculate selenium loads lost from the Delta through aqueducts. The seasonal loads were calculated by adding the daily loads. Estimated loads exported through aqueducts for the years between 1993-2003 range between 883 – 1,985 kg/yr (Figure 3-24). Dry season loads are comparable to wet season loads, largely because aqueduct exports are less variable than riverine flows over the course of the year. For a few years dry season loads exceed wet season loads (e.g. 1995, 1998). The range of annual exported loads using this approach is similar to what was determined previously, i.e., 700-2,700 kg/yr.

Contribution of loads to aqueducts from the two rivers was also estimated based on modeled contribution of flow from the two rivers and concentrations at each river. The results indicated that the San Joaquin River is the major, but not the only, source of selenium to the aqueducts. Estimated selenium loads from the Sacramento River are significantly lower ranging between 193-486 kg/yr for 1993-2003, compared to 600-1,780 kg/yr from the San Joaquin River. Although the Sacramento River dominates in terms of flow in the aqueducts most of the time, due to higher selenium concentrations, San Joaquin River contributes more selenium loads to aqueducts.

Assuming other losses are small, loads from the Delta to the bay can be estimated as the difference between total loads from the two rivers and the export through aqueducts. Estimated loads from the Delta to the bay show large variations among the years (1993-2003; Figure 3-25). Loads for dry years are approximately 1,000 kg/yr (e.g. 1994, 2001). Loads in wet years can be much larger (nearly 6,000 kg/yr in 1998). Contribution of loads from the two rivers to the Delta outflow was estimated as the difference between loads from the rivers and the export through aqueducts. Estimated loads from the two rivers to the Delta are generally comparable. Annual selenium loads from the San Joaquin River are normally below 1,000 kg/yr. However during wet years larger loads can originate from the San Joaquin River (exceeding loads from the Sacramento River). Dry season loads from San Joaquin River to the Bay normally range between 200-300 kg. However for a few wet years, dry season loads from the San Joaquin River are approximately 1,000 kg. An average dissolved selenium load of 2,696 kg/yr from the Delta to the bay for 1993-2003 was estimated using this method.

Observed selenium concentrations at Delta-Mendota Canal near Tracy Headworks (Milepost 3.50) obtained from U.S. Bureau of Reclamation are higher than the estimated selenium concentrations in the aqueducts using the flow-weighted method described above (Figure 3-23). Note the observed concentration at Delta-Mendota Canal has a high detection limit of 0.4 µg/L. Estimated loads in Delta-Mendota Canal near Tracy Headworks by Bureau of Reclamation are at 792-1279 kg/yr for water year 2002-2006. Given approximately equal export volume in the CVP and SWP, exported loads in aqueducts can range between 1580-2560 kg/yr. The range of loads is at the higher end of our estimates of 700- 2700 kg/yr.

Selenium concentration data from the State Water Project (SWP) aqueducts have been reported using relatively high detection limits. The SWP publishes data from monthly grab samples at the Banks Pumping Plant (<http://www.wmq.water.ca.gov/GrabSamplePage/GrabSampleTables/index.cfm>) with a detection limit of 0.001 mg/L or 1 µg/L, with most samples being below detection limits. These data were not used in the calculations.

3.4.4 Summary of Delta load calculations

Although loads from the Central Valley are a major source of selenium to NSFB, the estimation of these loads is not straightforward because of tidal influences at the edge of the Delta and the bay, and because of complexities caused by mixing and water export from the Delta. The load estimates are more difficult because of the limited data in the Delta and the aqueducts.

Our approach in this section was to apply three different methods to compute loads, and to compare these values. Note that for the second and third methods, data was available to compute only the dissolved selenium loads and not the total load.

- The first approach used average concentration of two RMP stations in the Delta and multiplies it by the net tidally corrected Delta outflow. This resulted in an annual average load estimate of 3,962 kg/yr of **total selenium** from the Delta to the NSFB (1994-2006).
- The second approach used selenium loadings from the Sacramento and the San Joaquin Rivers separately based on data from Cutter and Cutter (2004) and applied a “Delta removal constant” similar to Meseck (2002) to account for the possible selenium loss in the Delta. These concentrations were reported only as dissolved selenium, not total selenium. This resulted in an annual average load estimate of 2,493 kg/yr of **dissolved selenium** (1993-2003).
- The third approach was independent of the prior two: the loadings from Central Valley to the bay were estimated as the difference between inputs from the two rivers minus the export through aqueducts, and assuming minimal loss processes in the Delta. This resulted in an annual average load estimate of 2,696 kg/yr of **dissolved selenium** (1993 to 2003).

Given the simplifications and assumptions employed in these load calculations, and given that some loads are in terms of dissolved selenium, the range of annual averages is small, and the methods are supportive of one another. Because the data used in the analysis was most abundant for Method 1, and both total and dissolved data were available, and because the flow volumes used in load calculation are tidally corrected, it is recommended that this

method be used for describing Delta loads, resulting in an average Delta to bay export of 3,962 kg/yr.

Particulate selenium loads from the Delta to the Bay were estimated based on previously estimated TSS loads by Leatherbarrow et al. (2005a) or McKee et al. (2006) at Mallard Island. McKee et al. (2006) based on continuous monitoring data of SSC at Mallard Island to estimate TSS loads for water year 1995-2003. Reported TSS loads at Mallard Island vary greatly with water years ranging from 0.26 ± 0.08 Mt/yr (2001) to 2.6 ± 0.8 Mt/yr (1995). Particulate selenium concentrations average 0.62 ± 0.21 $\mu\text{g/g}$ ($n=5$) at the Sacramento River and 0.66 ± 0.42 $\mu\text{g/g}$ ($n=5$) at the San Joaquin River (Doblin et al. 2006). Therefore an average concentration of 0.64 $\mu\text{g/g}$ was used in the calculation for all years. As a result, estimated particulate selenium loads from Delta range between 151 – 1,510 kg/yr for 1995-2003 (mean: 698 kg/yr). The estimated loads are higher than those estimated by Abu-Saba and Ogle (2005) for November 1997 to November 1999 (47-686 kg/yr).

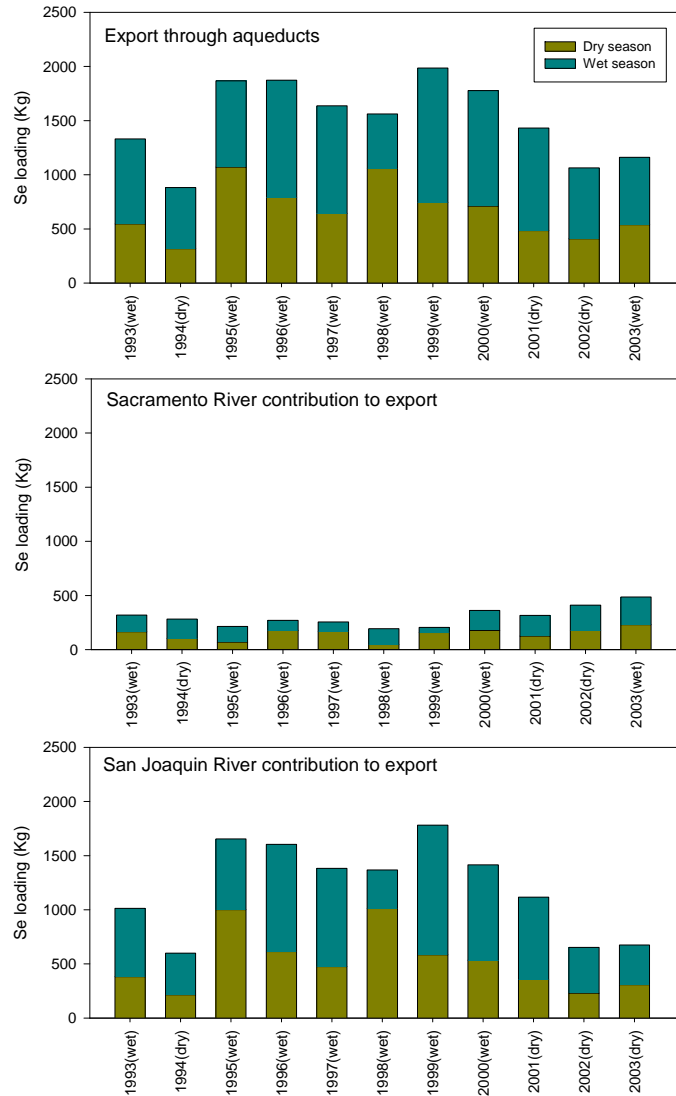


Figure 3-24 Estimated selenium loadings through the aqueducts and contributions from the Sacramento River and the San Joaquin River.

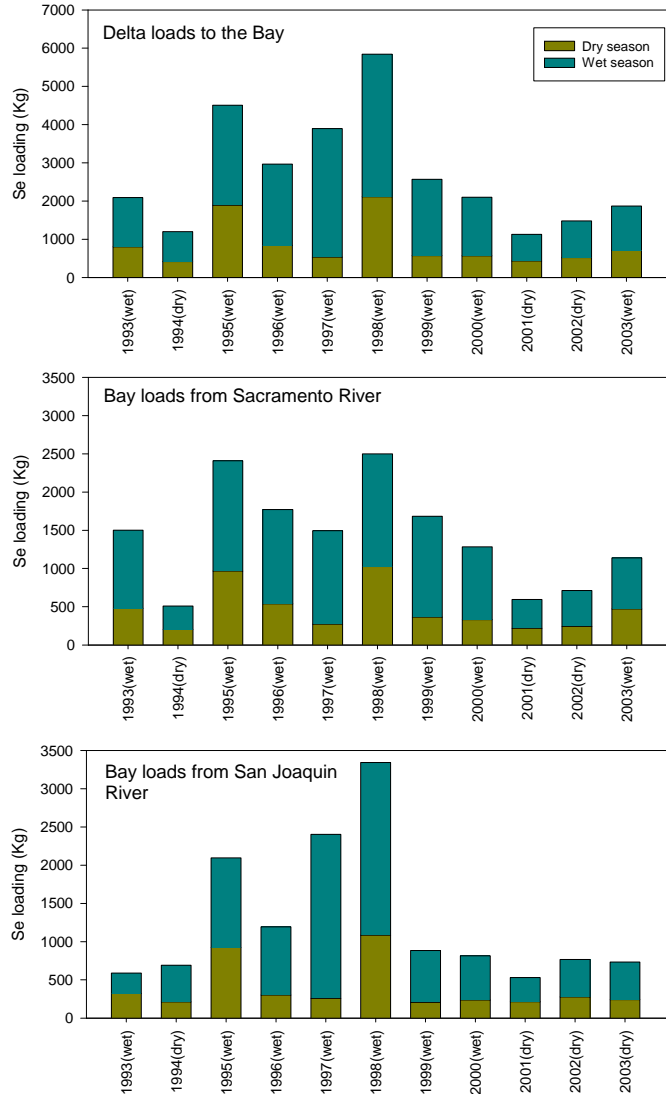


Figure 3-25 Estimated selenium loadings from the Delta to the Bay as the difference between loads from the Rivers and export through aqueducts, as well as contributions attributed to the Sacramento River and the San Joaquin Rivers individually.

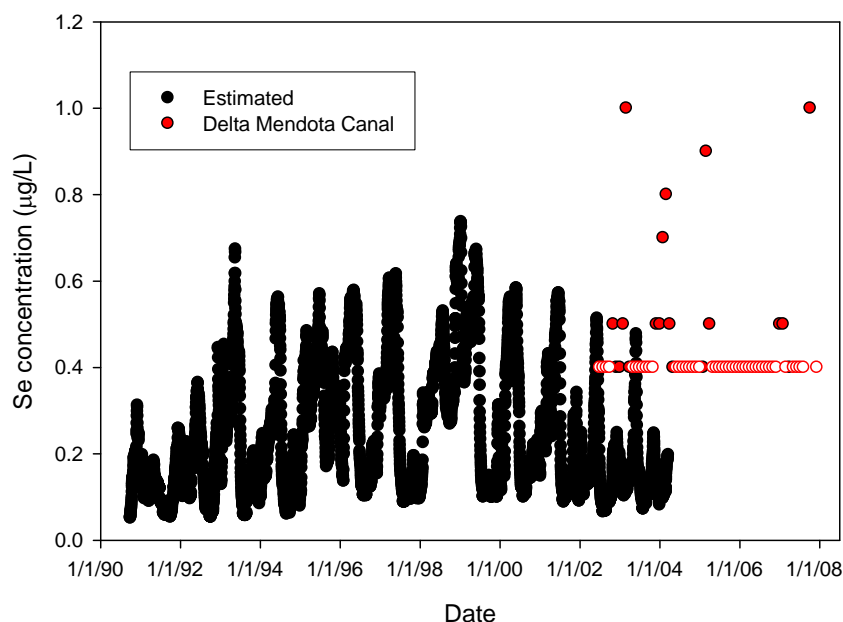


Figure 3-26 Estimated selenium concentrations in the aqueducts using flow weighted method compared to observed concentrations in Delta Mendota Canal near Tracy Headworks (MP 3.50) (Open circles indicates values below detection limit of 0.4 µg/L).

3.5. MUNICIPAL AND INDUSTRIAL WASTEWATER DISCHARGERS

Currently there are a total of 24 Publicly Owned Treatment Works (POTWs) located in the North Bay (Figure 3-27). Most of these facilities receive secondary treatment although a few incorporate advanced treatment (i.e., City of American Canyon, Napa Sanitation District). Dry weather flows from these facilities range from <1 to 120 mgd.

Flow at five largest municipal dischargers in the North Bay is shown in Figure 3-28. Flow at municipal discharges generally follows a seasonal pattern of higher concentration during the wet season, most likely due to storm water runoff. Concentrations in effluents of municipal dischargers generally are below 1 µg/L, with many samples below detection limit (Figure 3-29).

Effluent total selenium concentrations at a monthly interval are reported for these facilities. Total selenium concentrations in the effluents are generally near 1 µg/L (Table 3-11). Effluent concentrations at two facilities with the largest discharges (i.e., East Bay Municipal Utility District, EBMUD and Central Contra Costa Sanitation District, CCCSD) average 0.34 ± 0.19 µg/L and 0.34 ± 0.50 µg/L. Reported concentrations compared well to the dissolved selenium concentrations observed by Cutter and San Diego-McGlone (1990) during 1987-1988 sampling (24-hour composite sample at monthly intervals; CCCSD: 0.53 ± 0.11 µg/L, EBMUD: 0.37 ± 0.10 µg/L). No relationship between flow and concentrations in the effluent were observed. Therefore, no flow-concentration correlation was used in the load estimates.

Two methods were used in calculating daily loadings from POTWs. In the first method, the overall average daily maximum concentration was multiplied by overall average daily flow. In the second method, daily loadings were estimated based on flow and reported concentrations for all the available dates and an overall average of daily loadings was calculated. For concentrations reported as below the detection limit, concentrations were assumed to be half of the detection limit. Some non-detect data were reported with very high detection limits (e.g. 5 µg/L); in these cases data were disregarded. Estimated daily loadings show large temporal variations (Figure 3-30) related to the flow variability.

Estimated annual selenium loadings from POTWs in the North Bay are 255.3-255.8 kg/yr (Table 3-12). More detailed information on flows and concentrations, as well as identification of individual ports used in load estimates is presented in Appendix A5. The loadings are roughly half of values previously estimated by Cutter and San Diego-McGlone (1990) for the entire bay (1.08 kg/day or 394 kg/yr).

Effluents from municipal dischargers are dominated by selenate (60%), followed by selenite (25%) and organic and elemental selenium (15%; Cutter and San Diego-McGlone, 1990).

The second method used for POTWs was also used to calculate loadings from the industrial facilities in the North Bay. Loadings from industrial facilities are minor compared to other sources (Table 3-13).

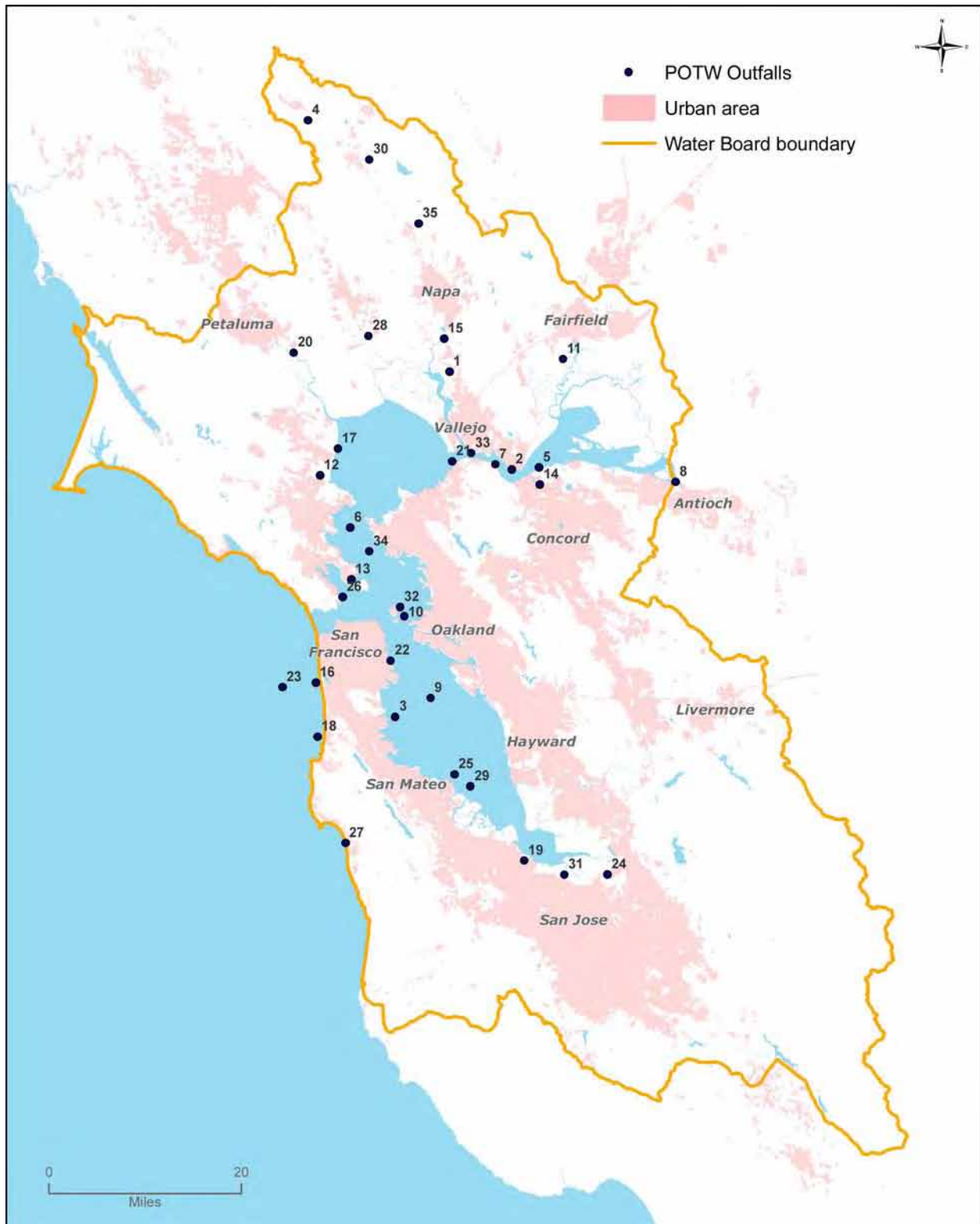


Figure 3-27 POTW discharge locations in and around San Francisco Bay (source: SFBRWQCB, Basin Plan).

Table 3-11
Summary statistics of daily maximum effluent concentrations at the municipal dischargers

Municipal dischargers	Outfall Location (Fig. 3-27)	Mean ¹	S.D.	Min	Max	Count
American Canyon (E-001-S)	1	1.16	0.59	0.2	2	32
City of Benicia	2	0.85	0.51	<0.3	5	98
City of Calistoga (E-001)	4	0.511	0.54	0.25	2.5	19
City of Saint Helena (E-001) ²	30	<0.5				
Central Contra Costa	5	0.34	0.50	<0.05	4	99
Central Marin Sanitation Agency	6	0.81	0.68	0.17	6.4	99
Delta Diablo	8	4.07	7.54	<1	37	104
EBMUD	10	0.34	0.19	<0.2	1.6	294
Fairfield-Suisun Sewer District	11	0.75	0.38	0	2	95
Las Gallinas Valley SD Permit	12	0.95	0.17	0.5	0.97	15
Marin Co. S.D. no. 5 (Paradise Cove) ²	13	0.73				
Marin Co. S.D. no. 5 (Tiburon)	13	1.93	1.40	0.5	6	47
Mount View Sanitary District	14	0.67	0.60	<0.02	5	38
Napa Sanitation District (dry)	15	0.57	0.21	<0.5	1	13
Napa Sanitation District (wet)	15	0.27	0.25	0	<1	26
Novato S.D (Ignacio Dry)	17	0.475	0.05	0.4	0.5	4
(Novato Wet)		0.833	0.32	0.4	1	4
City of Petaluma	20	0.65	0.23	0.35	1.4	60
Cities of Pinole-Hercules	21	0.91	0.66	<0.1	4	47
Rodeo Sanitary District	21	0.80	0.61	<0.1	3	30
Sausalito-Marin Sanitary District	26	2.46	0.91	0.5	17.5	85
Sewerage Agency of South Marin	13	1.39	2.01	0.15	12	133
Sonoma Valley County S.D.	28	<5.00	0.00	<5	<5	27
US Navy Treasure Island Permit	32	0.48	0.17	<0.25	8.96	46
Vallejo San & Flood Control District (Carquinez deep)	33	0.96	0.52	<0.7	10.6	79
West County/Richmond Permit	34	1.73	0.97	0.25	9	60

1. For values below detection limit, half of the detection limit was used in mean calculation.

2. Concentrations taken from permits

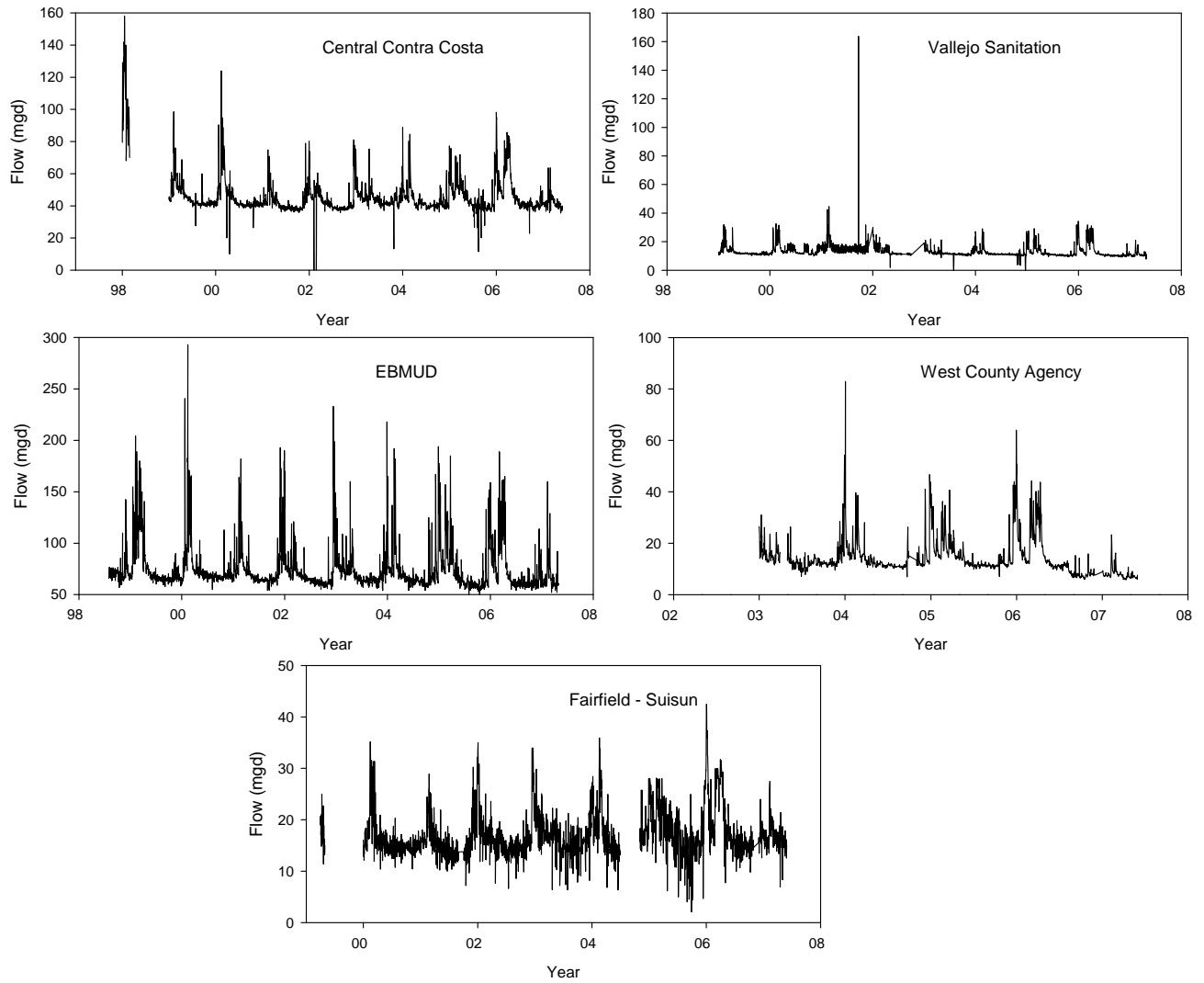


Figure 3-28 Daily effluent average flow at five largest dischargers in North Bay.

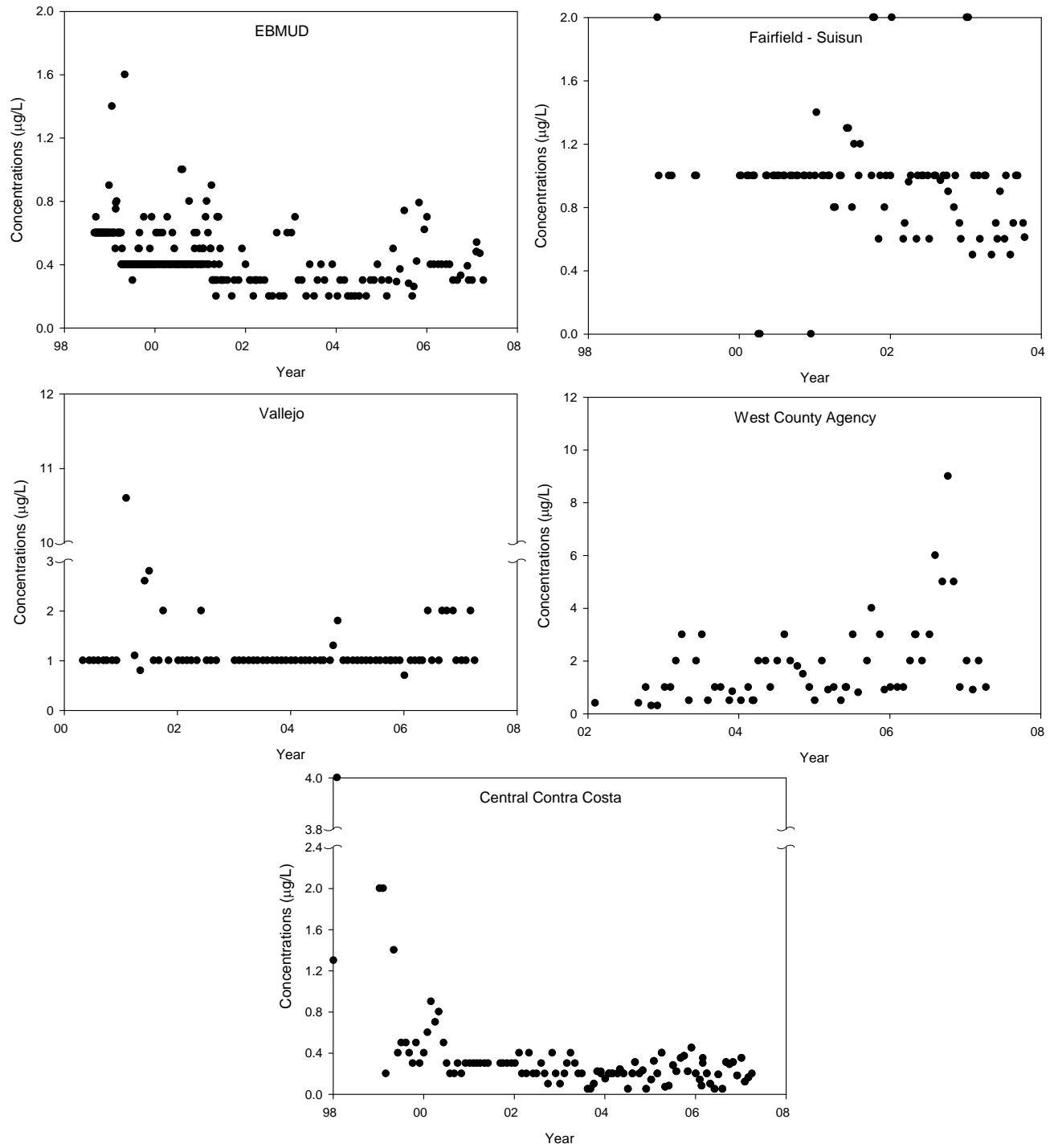


Figure 3-29 Effluent maximum concentrations for the five largest dischargers in the North Bay.

Table 3-12
Estimated total selenium loadings from POTWs in the North Bay

POTW Facility Name	Outfall Location	Average Flow (mgd)	Estimated Se Loadings ¹ (kg/yr)	Estimated Se Loadings ² (kg/yr)
City of American Canyon (E-001 S) (E-003 S)	1	0.89	1.42	1.53
		0.99	1.46	1.43
City of Benicia	2	3.0	3.5	3.4
City of Calistoga ³ (E-001 dry) (E-002 wet)	4	0.87	0.60	0.20
		0.65	0.46	
City of Saint Helena E-001 ³	30	1.11	0.38	
Central Contra Costa S.D.	5	45.8	21.8	15.0
Central Marin Sanitation A.G.	6	11.0	12.3	10.7
Contra Costa Co. S.D. no. 5 (Port Costa)	7	0.02	NA	NA
Delta Diablo	8	11.46	64.5	64.1
East Bay MUD	10	74.6	34.8	36.9
Fairfield Suisun Sewer Dist. (E-001 A) (E-004)	11	17.0	17.5	16.8
		1.44	1.48	1.68
Las Gallinas Valley S.D. (E-001) (E-002)	12	3.75	2.48	4.0
		1.44	0.95	
Marin Co. S.D. no. 5 (Paradise Cove)		0.02	0.73	
Marin Co. S.D. no. 5 (Tiburon)	13	1.02	2.72	1.86
Mount View S.D.	14	2.0	2.3	1.5
Napa S.D. (Dry weather) (Wet weather)	15	3.8	1.49	2.94
		13.98	2.60	10.34
Novato S.D. E-001 Ignacio Dry E-002 Novato Wet	17	4.01	2.63	2.90
		2.23	2.57	3.19
City of Petaluma	20	7.6	6.88	8.3
Cities of Pinole & Hercules	21	3.2	4.0	4.2
Rodeo S.D.	21	0.8	0.9	0.9
Sausalito-Marin City S.D.	26	1.6	5.5	4.9
Sewerage Agency of South Marin	13	3.3	6.36	5.10
Sonoma Valley County S.D.	28	4.1	--	High DL (5 µg/L) ⁴
U.S. Navy Treasure Island	32	0.5	0.4	0.25
Vallejo Sanitation & Flood Control (Carquinez deep) (Mare deep)	33	13.2	17.5	15.66
		2.69	2.85	7.56
West County Agency WCA (E-001 DC)	34	14.1	33.7	30.7
Total		243.9	255.3	255.8

1 - Estimated based on overall average concentration and average daily flow

2 - Estimated based on flow and concentrations on all available dates

3 - Not included in total load estimates due to distance from the Bay.

4 - Reported concentrations below high detection limit of 5 µg/L and load not estimated.

Table 3-13
Estimated selenium loadings from industrial wastewater dischargers in the North Bay

Industrial Facilities	Daily loading (g/day)	Annual loading (kg/yr)
Dow Chemical	6.5	2.4
General Chemical	4.8	1.8
GWF (I)	1.05	0.4
GWF (V)	0.4	0.1
USS-Posco	31.0	11.3
Total	43.7	16.0

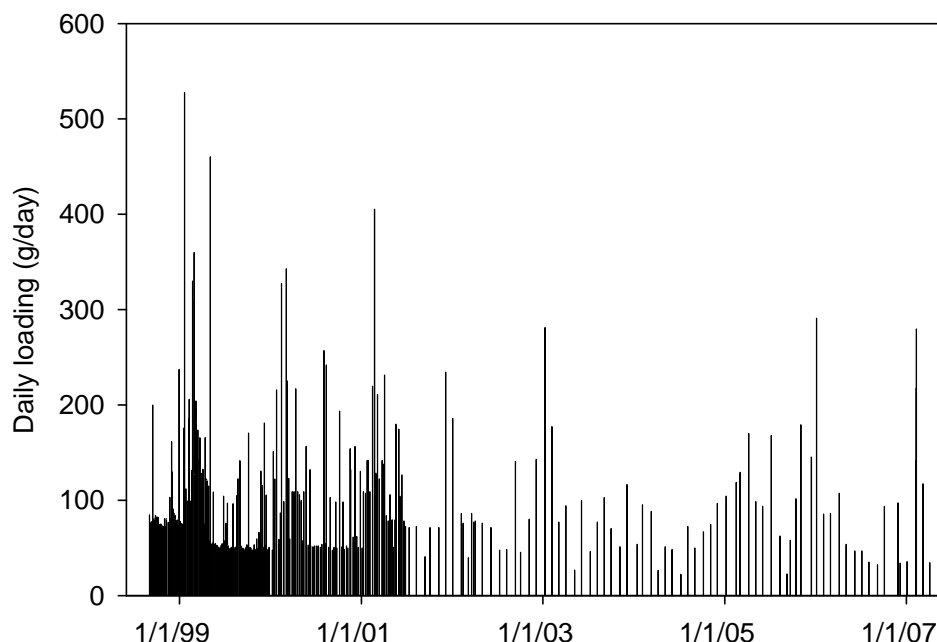


Figure 3-30 Estimated daily total selenium loadings from EBMUD.

3.6. PETROLEUM REFINERIES

Mean selenium concentrations at the refineries range between 11.9 – 27.7 $\mu\text{g/L}$ (Table 3-14). Concentrations show relatively large variations over time (Figure 3-31). Daily flow measurement at the refineries indicates some seasonal high flows, probably due to storm water runoff (Figure 3-32). Concentrations generally show no correlation with flow (Figure 3-33).

For the five petroleum refineries located in the North Bay, daily loadings were estimated based on the continuous daily flow data and the reported effluent daily maximum concentrations on a weekly basis. Mean daily maximum concentrations for the refineries range between 12 – 28 $\mu\text{g/L}$. No relationship between concentrations and flow were observed. The annual loadings were calculated by summing the daily loadings. The

estimated total daily loading from these refineries is 1.47 kg/day or an average of 537 kg/yr during 1999-2007 (Table 3-15). Current loadings are significantly lower than the previous years (1,407 – 3,382 kg/yr in 1986 – 1992) following the improvement in waste water treatment practices at the refineries (Presser and Luoma, 2006).

To calculate seasonal loads, daily loads were calculated by multiplying daily flow with weekly concentration extrapolated to the week and then adding up for dry and wet season. Wet season was defined as Oct. 1st to Apr. 30th. The dry season was defined as May 1st to Sep. 30th. Estimated annual selenium loadings are relatively constant throughout the years (Figure 3-34). Average dry season loadings are generally 62-78% of the average wet season loadings at four of the refineries. Average dry season loadings at Tesoro are only 35% of the wet season loadings.

The effluents are dominated by selenate (56%) and organic selenide (30%), with selenite accounting for only 14% on average (compared to 64% in 1987-1988, Cutter and Cutter, 2004). The speciation in refineries is similar to that in municipal wastewater effluents.

Table 3-14
Summary statistics of daily maximum effluent concentrations at the refineries

Refineries	Median	Mean	Standard deviation	Min	Max	Count
Chevron	11.2	12.1	5.9	2.3	48.0	308
ConocoPhillips (at Rodeo)	14.0	15.5	8.5	1.0	49.0	448
Shell Martinez	27.0	27.7	9.4	4.0	82.0	266
Tesoro	11.0	11.9	5.1	1.0	41.0	367
Valero	26.1	26.6	7.4	8.0	50.0	447

Table 3-15
Estimated total selenium loadings from petroleum refineries in the North Bay

Refinery	Flow (mgd)	Mean daily loading ¹ (kg/day)	Mean daily loading ² (kg/day)	Annual loading ¹ (kg/yr)	Annual loading ² (kg/yr)
Chevron	7.1	0.31	0.33	112.6	120.7
Conoco Philips	2.3	0.16	0.16	57.9	58.0
Shell Martinez	5.8	0.61	0.59	224.1	214.9
Tesoro	4.1	0.19	0.19	70.2	69.3
Valero	2.0	0.20	0.20	71.9	75.1
Total	21.3	1.47	1.47	536.7	538

1 – Calculated as continuous daily flow times weekly concentrations extrapolated to the rest of the week

2 – Calculated based on daily flow and concentrations on sampling dates only

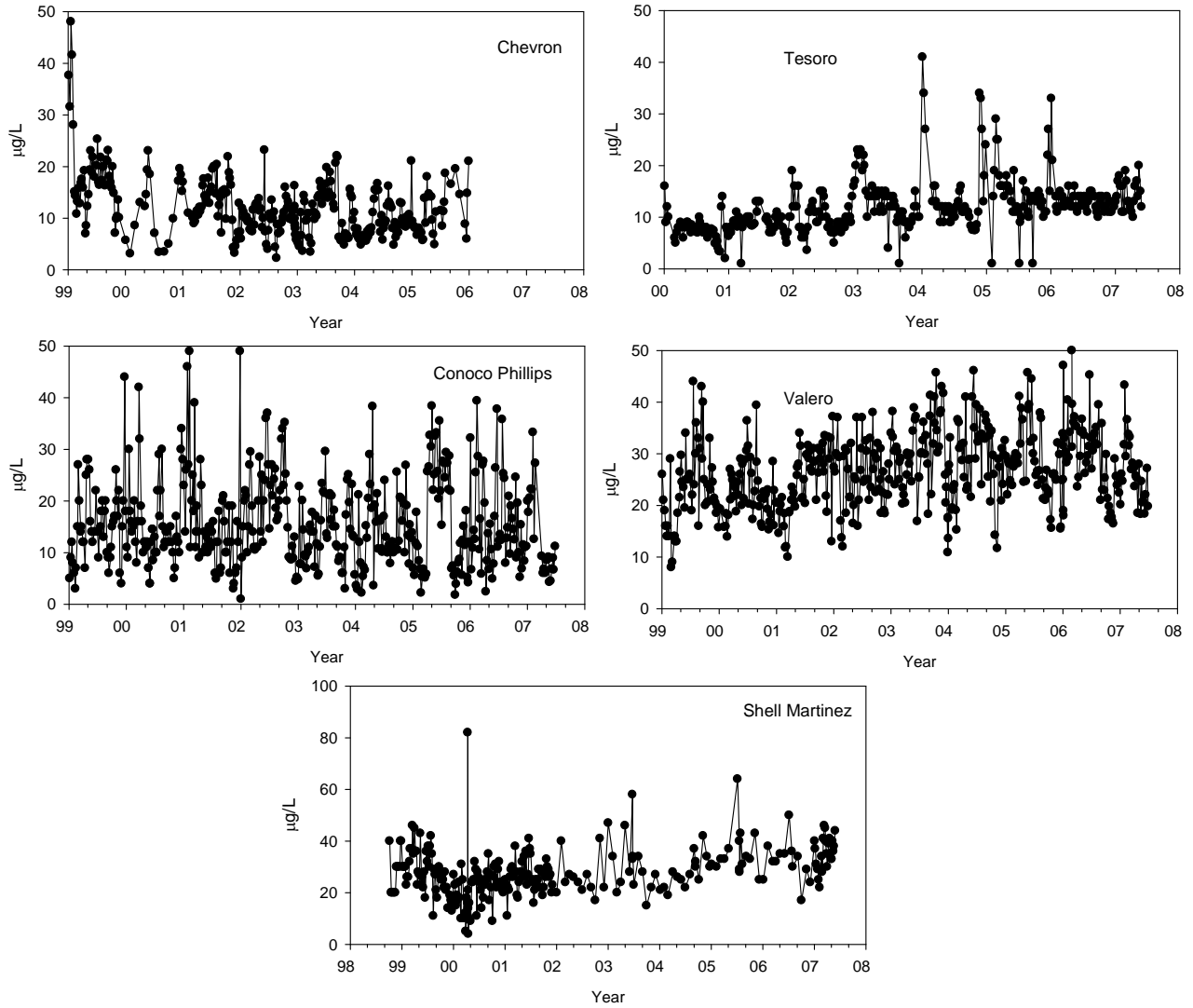


Figure 3-31 Effluent daily maximum selenium concentrations for the refineries in the North Bay.

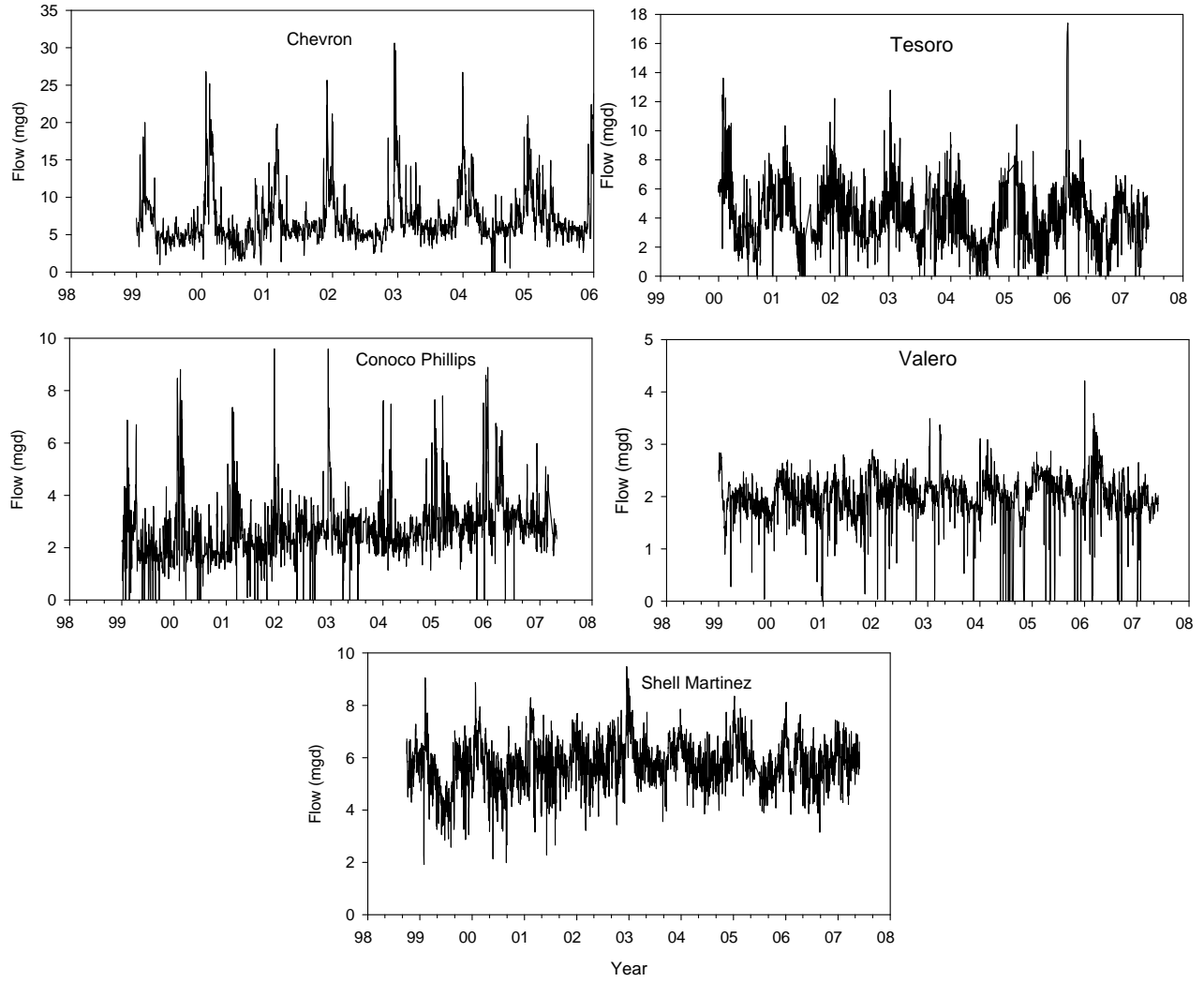


Figure 3-32 Daily average effluent flow rate from the refineries.

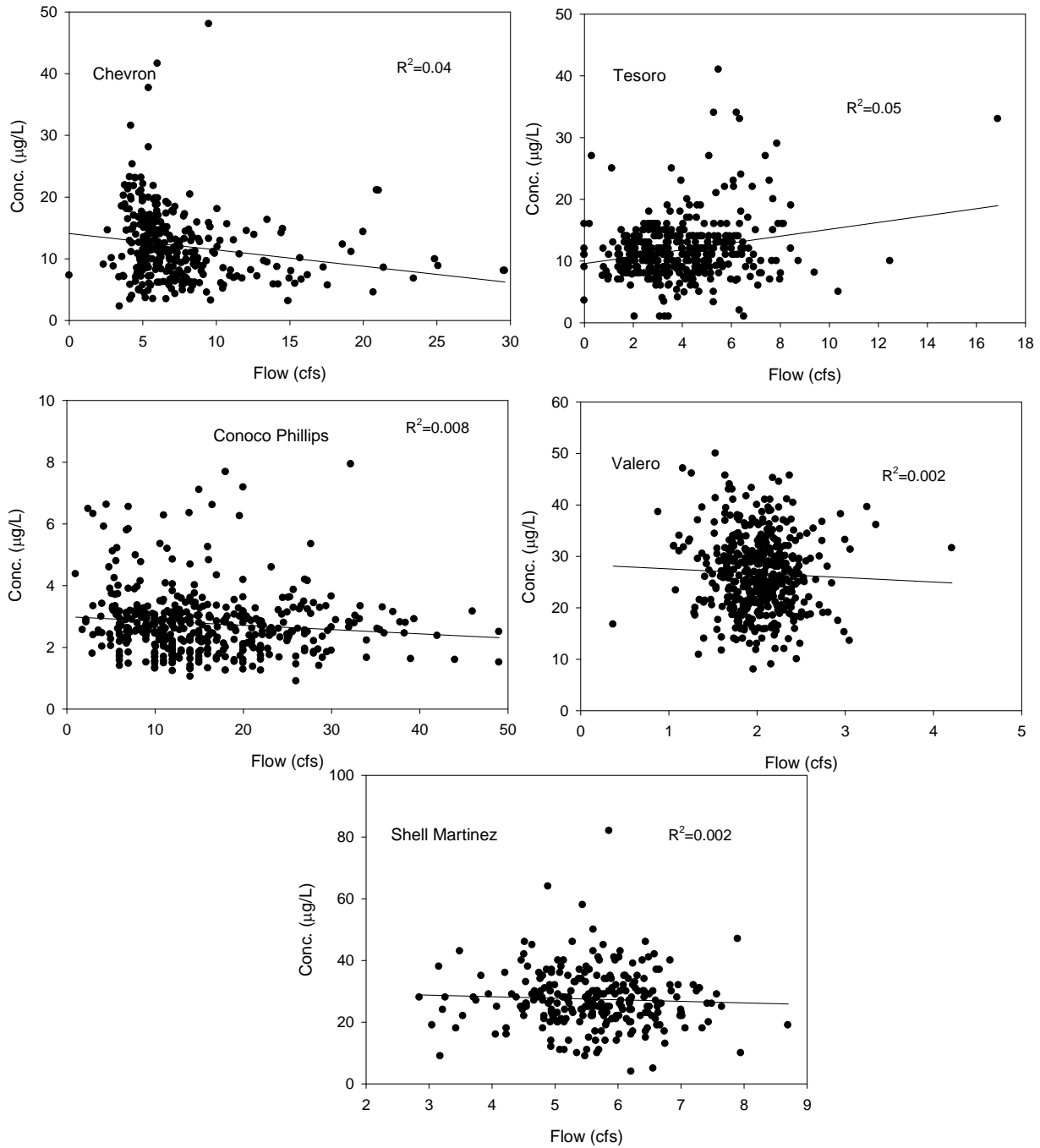


Figure 3-33 Concentrations and flow for the refineries in the North Bay. No meaningful correlations were found; the regression lines in the plots are to illustrate the lack of a relationship between flows and concentrations.

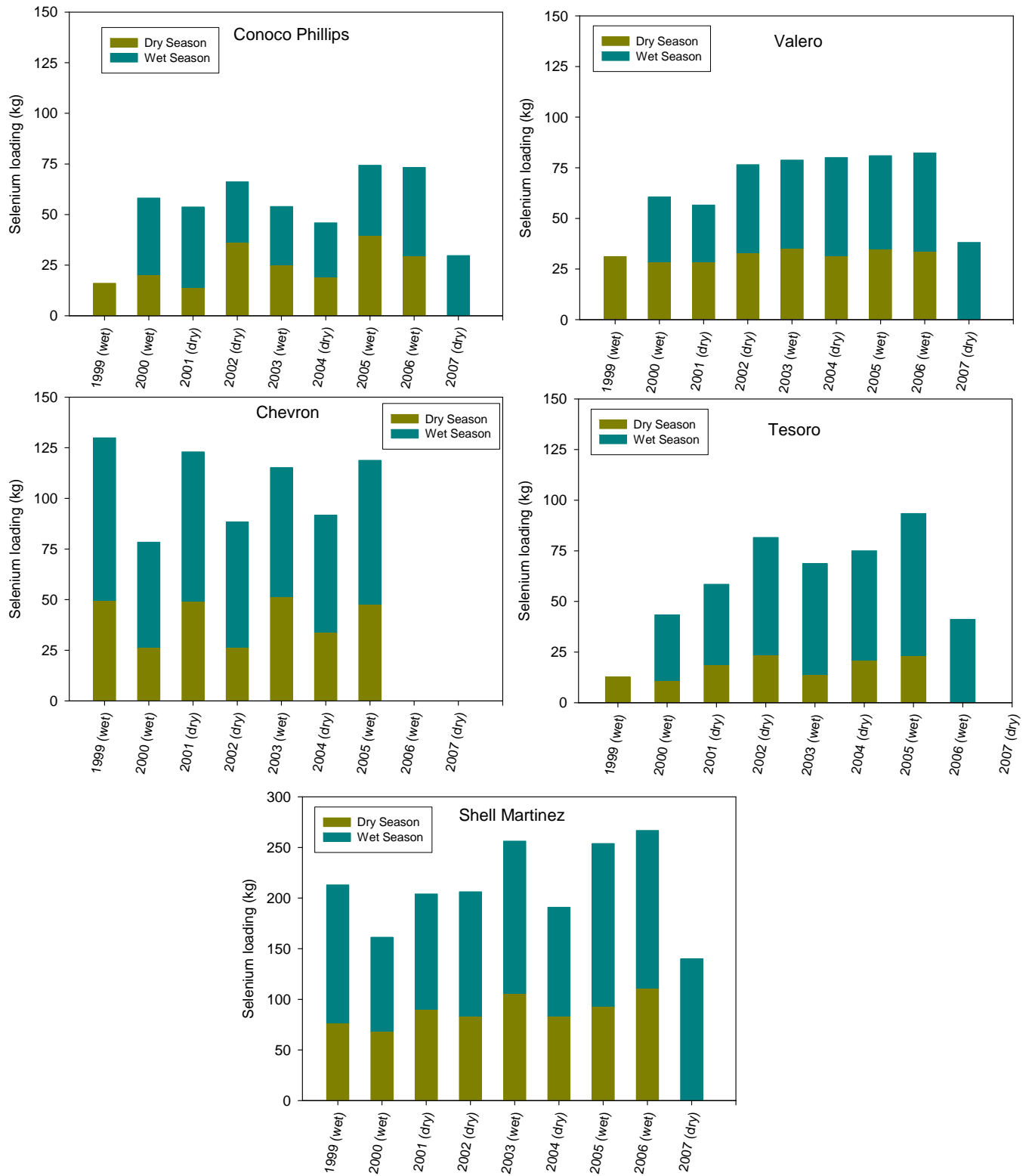


Figure 3-34 Dry and wet season selenium loadings from refineries for the years of 1999-2007.

3.7. INTERNAL SOURCES - SEDIMENT EROSION

Sediments in the North Bay represent a large reservoir of selenium (Abu-Saba and Ogle, 2005). A review of sediment processes in the San Francisco Bay indicated an active sediment mixing layer of 15 cm (Leatherbarrow et al. 2005b). Given the sediment mass for the upper 15 cm of the whole bay (1.4×10^{11} kg; Davis (2003), cited in Abu-Saba and Ogle, 2005) and mean selenium concentrations of $0.25 \mu\text{g/g}$, the selenium in the upper layer of sediments of North Bay is about 20,000 kg.⁵

Selenium in bottom sediments can be mobilized to the water column through resuspension, erosion, diffusion and bioturbation. Resuspension rates in the San Francisco Bay were found to be 2 to 5 times greater than the accumulation rates, indicating sediment is resuspended 2 to 5 times before settling (Leatherbarrow et al. 2005b). Previous studies indicated sediment residence time in the water column of 5 ± 3 days in San Pablo Bay. It was suggested that during summer low flow months, wind generated and tidal driven resuspension redistributes sediments to a wider area. Localized sediment erosion also occurs due to decreases in sediment supply from the surrounding watersheds. Net sediment erosion was found to occur both in the Suisun Bay and San Pablo Bay. For San Francisco Bay, the abundance of organisms has been found to potentially enhance mobilization of sediments to the water column. Diffusion of dissolved selenium from the sediment porewater to the water column has been found to be a small source, estimated at 18.2 kg/yr for the North Bay (Meseck, 2002). Direct biotic uptake of particulate selenium in bottom sediments by consumer organisms is another pathway of selenium mobilization, but this has not been quantified for the source analysis.

Selenium in sediments can also undergo a series of transformations (Meseck and Cutter, 2006). In deeper layers of sediment, selenate and selenite can be converted to elemental selenium due to microbial reduction. As a result, elemental selenium comprises a large portion of selenium in the sediments and the presence of elemental selenium in bay water can be an indicator of origin from bottom sediments. Organic selenide in surface sediment can also be oxidized to selenite and selenate or methylated by microbes.

Studies in San Pablo and Suisun Bay indicated that more erosion than burial is occurring in these two areas in the recent years (USGS 2001a, b). In Suisun Bay, net sediment erosion was 1-2 Mm^3/yr from 1887 to 1990 (USGS 2001a). During 1942 to 1990, Suisun Bay experienced a net loss of 61 Mm^3 of sediment, with a net loss of 1.27 Mm^3/yr at an erosion rate of 1.2 $\text{cm}/\text{m}^2/\text{yr}$. Erosion in San Pablo Bay is at a slower rate and only occurred after 1950s. San Pablo Bay lost approximately 7 Mm^3 of sediments between 1951 and 1983 at a rate of 0.22 Mm^3/yr (USGS 2001b). This net loss of sediments can be a potential source of selenium from sediments to the water column. Average selenium concentration in surface sediment is at $0.25 \mu\text{g/g}$. Sediment loss of Suisun and San Pablo Bay is estimated to be around 1,100 Mkg/yr (SFBRWQCB, 2004). This results in selenium loadings due to sediment erosion of 275 kg/yr.

⁵ Assuming North and Central Bay area of 434 km^2 and 214 km^2 , over the total area of 1133 km^2 for the whole Bay (Tsai et al. 2001).

Loss of tidal mudflats occurs both in fringe areas of Suisun Bay and San Pablo Bay (1000 acres in Suisun Bay during 1887 - 1990 and 125 acres/yr in San Pablo Bay). Loss of tidal mudflats may introduce contaminants previously deposited in these areas to the Bay (Marvin-DiPasquale et al., 2003).

Sediment dredging from navigation channels and disposal in locations inside and outside the bay can also influence sediment selenium pool. On average, in each year 1.8 million cubic yards of sediments were disposed in the bay and 2.4 million cubic yards were disposed out of the bay. Assuming a mean concentration of 0.25 µg/g, this represents a net loss of 82.5 kg/yr of selenium from the Bay (Table 3-16). In-bay disposal was estimated to be 248 kg Se/yr, while ocean disposal and upland/wetland reuse are 142.5 kg Se/yr and 225 kg Se/yr respectively. The dry mass of selenium was calculated assuming a particle density of 2.65 kg/L and a 50% solid per unit mass sediment, similar to assumptions used in the recent PCB TMDL for San Francisco Bay (SFBRWQCB, 2007c).

Table 3-16
Estimated selenium mass associated with dredge material disposal (2001-2005)¹

Disposal site	Total volume 2001-2005 (m ³)	Average volume (m ³ /yr)	Average annual estimated Se dry mass (kg/yr)
In-bay disposal	6,800,000	1,380,000	248
Ocean (SF-DODS) disposal	2,900,000	580,000	-142.5
Upland/wetland reuse	6,190,000	1,220,000	-225
Net loads			-82.5

¹Source of data for volume of dredge material is from SFBRWQCB, 2007c.

3.8. LOADS FROM THE SOUTH BAY

Water in the South Bay and Central Bay is subject to mixing near the Bay Bridge. As a result, selenium loads can enter the Central Bay from South Bay or vice versa. The net inflow of water is assumed to be equal to river flow from the South Bay (Smith and Holibaugh, 2006). To estimate the net effect of exchange between the two portions of the bay on selenium loads, we assumed selenium concentrations at a station near the boundary of the two bays (BC10 Yerba Buena Island) to be representative of net inflow concentration from the South Bay. Estimated freshwater inputs from local watersheds of South Bay are 664 Mm³/yr (Davis et al. 2000). With the mean selenium concentration of 0.16 µg/L at Yerba Buena Island (Table A-3), estimated selenium inputs from South Bay to the Central Bay is at 106.2 kg/yr. The estimated load is relatively small compared to other selenium sources to the North Bay.

One of the tributaries in the South Bay, the Guadalupe River can be a major source of selenium to the South Bay because of high concentration. Observed average total selenium concentration at Guadalupe River (BW15) by RMP is at 4.76 µg/L. With the annual flow of 39.9-141.9 cfs for 2003-2007 (USGS11169025), selenium loads from this tributary alone can be 169.6-603.2 kg/yr. Therefore, the estimated 106.2 kg/yr load from South Bay may be at the lower bound of the loads entering from South Bay or suggests that significant removal of selenium via deposition may be occurring in the South Bay.

3.9. COMPARISON OF SELENIUM CONCENTRATIONS AND LOADS FROM DIFFERENT SOURCES

A comparison of total and dissolved selenium concentrations from several sources of interest is summarized in Table 3-17. In terms of concentrations, the refineries have the highest selenium concentrations compared to other sources such as Delta outflow, atmospheric deposition, municipal wastewater and the bay water, followed by local tributaries.

A comparison of relative importance of loadings from various sources is listed in Table 3-18. Input from Delta represents the largest source of total selenium and exhibits large variation depending on flow. Local tributaries and refineries are other two important sources. Loadings from atmospheric deposition and municipal wastewater are smaller. Bay sediment erosion contributes a notable portion of the particulate selenium loadings.

Table 3-17
Representative selenium concentration in different sources

	Source	Total (µg/L)	Dissolved (µg/L)
Atmospheric deposition	Mosher and Duce (1989)	-	0.1-0.4
Local tributaries (data for individual tributaries)	SFRWCB, 2007a,b	0.4-4.0 ¹	0.3-3.9
	BASMAA (1996)	0.46	
Municipal wastewater	Data provided by SFBRWQCB	<1	-
Refineries	Data provided by SFBRWQCB	12-28 ²	12-28
Mallard Island (outflow from Delta) Storm Values	L. McKee, personal communication	0.46	-
San Joaquin River @ Vernalis (1999-2000)	Cutter and Cutter (2004)		0.68
Sacramento River @ Freeport (1999-2000)	Cutter and Cutter (2004)		0.07
San Joaquin River near Mallard Island (BG30)	RMP	0.18	0.16
Sacramento River near Mallard Island (BG20)	RMP	0.15	0.13
Bay water (1993-2005)	RMP	0.18	0.15

1. Mean of downstream sites in North Bay (SFRWCB, 2007a, b), Table 3-2

2. Mean concentrations at individual refineries listed in Table 3-1.

Table 3-18
Relative importance of loadings from different sources

	Total (kg/yr)	Dissolved (kg/yr)	Particulate (kg/yr)	Uncertainty
Sources:				
Atmospheric deposition	17.8-163.5	13.7 – 78.1	4.1-85.4	High
Local tributaries	354 -1511 (354-834 best estimate)	-	118.2 ¹	High
Municipal and industrial wastewater	255	-	-	Low
Refineries	538	-	-	Low
Input from Delta	1,110-11,752 (mean:3,962)	814-9,736 (mean: 3,354)	151-1,509 ² (mean: 698)	Moderate
Sacramento River at Freeport		670-2,693 (mean: 1,577) for 1991-2007		Moderate
San Joaquin River at Vernalis	760-7,270 ⁵ (mean: 2,972) for 1994-2007	838-4,711 (mean: 2,289) for 1991-2007		Moderate
Sediment	293	18.2 ⁴	275	Moderate
South Bay	106			High
Sinks:				
Outflow	4500 ³	3750 ³	750 ³	Moderate
Sediment Dredging	82.5	82.5		Moderate

¹Based on TSS loadings by Davis et al. (2000), times selenium content in particulate material of Sacramento River

²Based on TSS loadings by McKee et al. (2006) and mean selenium content in particulate material of Sacramento and San Joaquin Rivers

³Based on average Delta outflow of 25000 Mm³. Outflow only includes loads contributed by the northern reach.

⁴Sediment diffusion rate estimated by Meseck (2002).

⁵Based on SWAMP dataset

A comparison of dry and wet season loadings from different sources (Table 3-19) indicates that during the dry season, the major source of selenium loadings is from the Delta. The local tributary contribution during the dry season is minimal. During the wet season, the Delta outflow and local tributaries are the main selenium sources to the Bay. Refineries have a relatively steady input during both dry and wet seasons.

Table 3-19
Summary of dry and wet season selenium loading from major sources

	Dry season (kg)	Wet season (kg)	Annual total (kg)
Delta (Total, RMP data)	1,007.4	2,930.7	3,938.2 (total)
Delta (Dissolved, assuming 60% removal of San Joaquin River load)	909.5	1,583.1	2,492.6
Sacramento River at Freeport	564.1	1,012.7	1,576.9
San Joaquin River at Vernalis	863.4	1,426.0	2,289.4
Export through aqueducts	664.5	841.7	1,506.1
Delta (dissolved, difference between river loads and export through aqueduct)	855.5	1,840.4	2,595.9
Tributaries ¹	75.8	1,434.8	1,510.6
Refineries	204.2	322.2	526.4

¹ Estimates from Method 2

The estimated selenium loads from different sources were compared to previous studies of Presser and Luoma (2006), Meseck and Cutter (2006) and Abu-Saba and Ogle (2005) (Table 3-20). Selenium loads from refineries compared well to loads estimated by Presser and Luoma (2006) and Abu-Saba and Ogle (2005). Loadings from the Delta on an annual basis were also comparable to estimates of Presser and Luoma and in the same range of Abu-Saba and Ogle (2005), principally because the estimated range is wide. However, dry season Delta to bay loads in this work are substantially higher than previous estimates by Presser and Luoma (2006): over 1,000 kg compared to 200 kg. Loadings from local tributaries were higher than estimates by Abu-Saba and Ogle (2005), most likely due to higher selenium concentrations and runoff values used in the calculation.

Table 3-20
Comparison of alternative total selenium loadings estimates to North San Francisco Bay.

Source Category	Presser and Luoma (2006)	Meseck and Cutter (2006)	Abu-Saba and Ogle (2005)	This report
All loads in kg				
Refineries: Prior to improved wastewater treatment in 1998, kg/yr	1,850	2,890	610-1,660	No estimate
Refineries: Subsequent to improved wastewater treatment in 1998, kg/yr	620 ¹	1,100	204-552	526
Delta loads, kg/yr	200 kg/6 months, critically dry season; 4,500 kg/6 months, high flow season	No estimate reported; value embedded in model calculations.	330-10,200 (Nov 1997- Nov 1999)	3,946 annual average; 1,007 dry months and 2,930 wet months
Selenium inventory in sediment bed, kg	No estimate	No estimate	50,000 in upper 15 cm of entire San Francisco Bay	20,000 kg in top 15 cm in North San Francisco Bay
Sediment erosion	No estimate	No estimate	No estimate	293
Local tributaries and waste water to North San Francisco Bay, kg/yr	No estimate	No estimate	90-900 (to all San Francisco Bay)	Local watershed runoff: 354-834
POTWs	No estimate	No estimate	90-900	Wastewater, other than refineries: 255
Atmospheric deposition, kg/yr	No estimate	No estimate	No estimate	18-164

¹From the value illustrated in Figure 26 (p93) of Presser and Luoma (2006). The number 506 kg/yr on page 1-1 was from Table 10 (p35) of Presser and Luoma (2006) where the actual loads were estimated for 1999.

3.10. LOW FLOW VS. HIGH FLOW CONCENTRATIONS

Selenium loadings and concentrations in water column and the suspended particulate material can vary with flow conditions. Under high flow, high loadings from Delta combined with short residence time can result in selenium concentrations in the bay that are similar to those in Delta inflows. During low flow periods, local sources from point dischargers may become a larger source. Under low flow, also due to the longer residence time and warmer temperature, selenium is more likely to accumulate in phytoplankton and bacteria. Zooplankton selenium concentrations have been found to be highest during low flow period (Pukerson et al. 2003). Therefore the low flow season is a critical time period for selenium bioaccumulation. The hydraulic residence time in NSFB can vary from 2 days during high flow to an average of 160 days during low flow (Cutter, 1989).

To forecast the expected selenium concentrations in water column and suspended particulate material, a simple, completely-mixed, one-box model similar to Presser and Luoma (2006) was used to estimate possible concentrations in the bay under several flow conditions: high flow in a wet year (2006), low flow in a wet year (2006), and low flow in a critically dry year (2001). Loadings from various sources estimated in previous sections were used.

Partition coefficient between dissolved and particulate selenium were derived from data of Doblin et al. (2006).

Several processes besides outflow to ocean that may contribute to the selenium removal: methylation to form dimethylselenide followed by volatilization, influx of dissolved selenium into sediments, reduction followed by adsorption and settling, phytoplankton uptake, and settling of suspended sediment. Previous study has indicated that diffusion into and out of the sediment is negligible (Mesnick, 2002). Due to the oxic water, reduction of selenium is less likely to occur in the water column. Sediments in Suisun and San Pablo Bay are erosional, therefore net deposition into sediments are unlikely to be an important removal mechanism. More details of the one-box model are provided in the Appendix.

Predicted mean selenium concentrations using zero removal rates under high flow are generally similar to the observed concentrations from the RMP random sampling during 2002-2005 (0.14 µg/L; Table 3-21), suggesting relatively conservative behavior during high flow. Predicted maximum selenium concentration under low flow of a critically dry year is at higher concentration of 0.36 µg/L. RMP sampling during a representative period in August 2001 indicated a North Bay average of 0.15 µg/L. Because the observed concentrations during this period are significantly lower than predictions with removal rates set to zero, removal process may indeed be significant during these periods. The one-box modeling described here is a preliminary effort to assess the data and will be refined in subsequent work on the conceptual model and detailed mechanistic model.

Table 3-21
Estimated selenium concentrations under different flow conditions (more detailed calculation listed in Appendix A).

	Delta outflow (Mm³/day)	Delta loadings (kg/day)	Loadings from other sources* (kg/day)	Predicted total selenium concentrations (µg/L)	Concentrations in suspended particulate material** (µg/g)
High flow, wet year (2006)	202.2	19.0	9.6	0.14	0.94
Low flow, wet year (2006)	73.0	6.9	3.2	0.14	0.92
Low flow, critically dry year (2001)	14.2	2.0	3.2	0.33	2.20

*includes loadings from refineries, POTWs, local tributaries (proportional to delta outflow), and bed erosion.

**based on average K_d of 7.4 L/g (Cutter and Cutter, 2004).

4. SUMMARY

In this analysis selenium concentrations in water column and sediment were examined to provide a baseline for future modeling to be performed as part of the selenium TMDL in North San Francisco Bay. Major sources of monitoring data are the RMP and Prof. Greg Cutter's research group at Old Dominion University. The RMP has obtained selenium data at regular intervals at fifteen stations in the North Bay between 1993 and 2002, at 12 random stations for water concentrations and at 24 stations for sediment concentrations between 2002 and 2005. Selenium concentrations are generally low in the Bay water column with a whole North Bay average of 0.12 µg/L. Selenium concentrations in sediments are generally below 0.3 µg/g. Concentrations are lowest near the Golden Gate Bridge, with higher concentrations at lower salinities. More focused data sets that spanned a longer time frame and contained speciation data were also evaluated (Cutter, personal communication, 2007). The data show that there have been significant decreases in dissolved selenium concentrations and selenite in the North Bay since the mid-1980s, particularly in the low-flow season, following the implementation of more stringent controls on refinery discharges. Much of the selenium in the waters of the bay is in dissolved form, and consists of selenate, selenite, and organic selenide.

The quantification of selenium loadings from different point and non-point sources including Sacramento River and San Joaquin River inputs through Delta, local refineries, POTWs, tributaries and sediments, during both dry and wet season, was another major component of this analysis. The results indicated that annual loadings from the Central Valley through the Delta are the largest source of selenium with high variability depending on total flow through the Delta. Concentrations from the RMP stations are weakly correlated to Delta outflows to the bay, and therefore loads in high flow years are estimated to be more than ten times higher than in low flow years. The average Delta load is estimated to be 3,962 kg/yr. Local tributaries draining both urban and non-urban areas are also a large source of selenium (estimated average load of 354-834 kg/yr). Refineries are now estimated to be the third largest source of selenium to the North Bay (538 kg/yr), although these loads may have been higher prior to the late 1990s when wastewater controls were installed. Sediment resuspension/erosion and diffusion (293 kg/yr), other wastewater discharges (250 kg/yr), and atmospheric deposition (18-164 kg/yr) are other, smaller contributors of total selenium load. The point source loads (the refineries and the POTWs) contribute relatively uniform loads over the year, although the non-point source loads (the Delta and the local tributaries) contribute substantially more load in the wet season than in the dry season.

Although numerical values of load estimates are provided here for comparison, it should be acknowledged that this process contains significant uncertainty, and more than one estimation method may be applied, sometimes leading to different answers as described below. This is particularly true of non-point source load estimates. These alternative values are described below for completeness.

Selenium loads at Sacramento and San Joaquin River were estimated based on data collected by Cutter and Cutter (2004). Sacramento River at Freeport was estimated to have an average annual dissolved selenium loading of 1,577 kg/yr for 1991-2007. San Joaquin River at Vernalis has an average of dissolved selenium loading of 2,289 kg/yr for 1991-2007.

We applied three different methods to compute loads, from the Delta to the bay, depending on available data:

- The first approach used average concentration of two RMP stations in the Delta and multiplies it by the net tidally corrected Delta outflow. This resulted in an annual average load estimate of 3,962 kg/yr of **total selenium** from the Delta to the NSFB (1994-2006).
- The second approach used selenium loadings from the Sacramento and the San Joaquin Rivers separately based on data from Cutter and Cutter (2004) and applied a “Delta removal constant” similar to Meseck (2002) to account for the possible selenium loss in the Delta. These concentrations were reported only as dissolved selenium, not total selenium. This resulted in an annual average load estimate of 2,493 kg/yr of **dissolved selenium** (1993-2003).
- The third approach was independent of the prior two: the loadings from Central Valley to the bay were estimated as the difference between inputs from the two rivers minus the export through aqueducts, and assuming minimal loss processes in the Delta. This resulted in an annual average load estimate of 2,696 kg/yr of **dissolved selenium** (1993 to 2003).

In addition to these loads, the average particulate load was estimated as 698 kg/yr, based on loads of sediment from the Delta to the bay and by application of a constant selenium content in the sediments.

Given the simplifications and assumptions employed in these load calculations, and given that some loads are in terms of dissolved selenium, the range of annual averages is small, and the methods are supportive of one another. Because the data used in the analysis was most abundant for Method 1, and both total and dissolved data were available, and because the flow volumes used in load calculation are tidally corrected, it is recommended that this method be used for describing Delta loads, resulting in an average Delta to bay export of 3,962 kg/yr.

Using the SWAMP selenium data from the tributaries, loads were computed using flow from different sources: modeled annual flows and measured flows from USGS gage stations. The modeled flows were used because of the limited availability of measured flow data. Driven in large part by relatively high concentrations in the tributaries in both the wet and dry seasons, the average annual loads from the tributaries can range from 354 kg/year to 1,511 kg/year depending on the methods used for the load estimation. Much of this load (greater than 95%) is delivered to the bay in the wet months, consistent with the timing of flows, as shown in the calculation using the USGS gage data. The largest single sources of loads are the Napa River, Sonoma Creek, and the Concord hydrological area.

Although the tributary concentration data are different between two datasets (SWAMP and BASMAA), the high average concentrations are not driven by one or two measurements. It is nonetheless clear that the load estimates above are based on a limited amount of data. Furthermore, the SWAMP concentration data are not independently corroborated. Given the underlying data limitations and uncertainty in flows, and the year-to-year variability, the

wide range in the load estimates are not entirely surprising. For the purpose of this analysis, we recommend using a range of load estimates for the next stage of the analysis of 354-834 kg/yr.

5. KEY FINDINGS AND IMPLICATIONS FOR MODEL DEVELOPMENT

The analysis presented here is an important first step in the modeling to be performed for the selenium TMDL. Key findings from this analysis, including uncertainties and data gaps, that will carry forward to the next steps are listed below:

- More than two-thirds of the selenium in bay waters is present in the dissolved form, with the majority in the selenate form.
- Selenium concentrations vary according to the freshwater flows moving through the bay, and are highest in the in the mid-estuarine regions in the driest periods of the year.
- Sediment selenium concentrations from the RMP data set, averaged over several years of sampling at fixed stations, vary over a narrow range 0.2 to 0.5 $\mu\text{g/g}$, with a few exceptions. These concentrations correlated well with TOC and percent fines. Almost all sediment data have been collected near the surface (15 cm deep or less). No data are available to estimate natural background levels of selenium in the bay sediments.
- Refinery load reductions are consistent with reductions in selenium concentrations in NSFB in both wet and dry seasons. Concentrations of selenite, a major component of refinery discharges in the past, show dramatic declines from 1998.
- Local tributary selenium concentrations are high (i.e., closer to San Joaquin River values than Sacramento River values) and result in significant loads to the NSFB, although more than 95% of this load is delivered in the wet months. The data used in this calculation have been collected by the SWAMP program and have not been corroborated by other monitoring programs. The Napa River was estimated to be the largest tributary load contributor. A sediment sample in the bay near the mouth of the Napa River showed significantly elevated concentrations.
- Selenium loads in NSFB are dominated by non-point sources, and therefore correlated with runoff. Because of the region's climate, with distinct seasonal patterns of rainfall, and significant variability from year to year, the non-point loads are highly variable both on a seasonal and annual basis.
- Load estimates of the rivers to the bay showed that both San Joaquin and Sacramento Rivers are significant contributors of selenium to the NSFB. Their load contributions are of similar magnitude and occur in both wet and dry seasons.
- The large Central Valley selenium sources are transported through the Delta, but data within the Delta are limited, and understanding of its role in the removal and/or export of selenium is based on a small amount of data.
- Point source loads (refineries, POTWs, and other industrial dischargers) are among the best characterized loads in to NSFB because both flow and concentration are measured simultaneously. These loads are also less variable through the year and the wet season and dry season loads similar. This contrasts with Delta loads and tributary loads which are far larger in the wet months. On an annual basis, point

source loads are relatively small; on a seasonal basis, point source loads are significant during the dry months.

- POTW discharge concentrations of selenium are much smaller than refinery wastewater concentrations. However, because their flows are larger, on a load basis, POTW loads are about a third of the refinery loads.

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APPENDICES

Table A-1
Parameters and inputs of one-box model

Category	Value	Unit	References
Water depth (mean)	6.1	m	Conomos et al. 1985
Surface area			
North Bay	434	km ²	Tsai et al. 2001
Central Bay	214	km ²	Tsai et al. 2001
Volume			
North Bay+ Central Bay	3953	Mm ³	Calculated
Delta outflow			
Wet year (2006), wet season average	202.2	Mm ³ /day	http://iep.water.ca.gov/dayflow/
Wet year (2006), dry season average	73.0	Mm ³ /day	http://iep.water.ca.gov/dayflow/
Critically dry year (2001), dry season	14.2	Mm ³ /day	http://iep.water.ca.gov/dayflow/
Delta loads			
Wet year (2006), wet season	19.0	kg/day	Average of daily loads
Wet year (2006), dry season	6.9	kg/day	Average of daily loads
Critically dry year (2001), dry season	2.0	kg/day	Average of daily loads
Refineries loads (wet season)	1.53	kg/day	
Refineries loads (dry season)	1.36	kg/day	
Bed erosion	0.75	kg/day	
Local tributaries (wet)	6.80	kg/day	
Local tributaries (dry)	0.57	kg/day	
Local tributaries (dry, 2001)	0.14	kg/day	Scaled from Napa 2001 dry season loads
Wastewater	0.50	kg/day	
Residence time			
Wet year (2006), wet season	19.5	day	Calculated
Wet year (2006), dry season	54.2	day	Calculated
Critically dry year (2001), dry season	278.4	day	Calculated
Predicted mean concentrations (total)			
Wet year (2006), wet season	0.14	µg/L	
Wet year (2006), dry season	0.14	µg/L	
Critically dry year (2001), dry season	0.33	µg/L	
Concentrations in particulates			
Wet year (2006), wet season	0.94	µg/g	
Wet year (2006), dry season	0.92	µg/g	
Critically dry year (2001), dry season	2.2	µg/g	

Equations: Assuming completely mixed and steady state:

(1). $C = W/a$, where W: loadings from all sources, a: assimilation coefficient, C: concentration

(2). $a = Q + kV + vAs$, where Q: outflow, k: degradation/reaction coefficient, v: settling velocity, As: surface area. For simplicity, k and v are assumed to be 0.

(3) $C_s = K_d \cdot C_w$, where C_s : concentration in particulate, K_d : partition coefficient, C_w : dissolved concentration. C_w is assumed to be 90% of C .

Table A-2
Summary of dissolved selenium concentrations in water for the period of 1993-2005 for the whole Bay (data source: RMP).

Site Code	Site Name	Median (µg/L)	Mean (µg/L)	Standard Deviation	Count
BA10	Coyote Creek	0.37	0.43	0.21	21
BA20	South Bay	0.33	0.32	0.12	23
BA30	Dumbarton Bridge	0.25	0.26	0.09	28
BA40	Redwood Creek	0.17	0.18	0.05	24
BB15	San Bruno Shoal	0.15	0.16	0.07	20
BB30	Oyster Point	0.13	0.16	0.09	24
BB70	Alameda	0.12	0.16	0.18	19
BC10	Yerba Buena Island	0.11	0.14	0.08	27
BC20	Horseshoe Bay	0.10	0.14	0.10	23
BC30	Richardson Bay	0.13	0.14	0.10	23
BC41	Point Isabel	0.10	0.14	0.09	24
BC60	Red Rock	0.12	0.15	0.10	20
BD15	Petaluma River	0.17	0.18	0.07	21
BD20	San Pablo Bay	0.14	0.15	0.06	24
BD30	Pinole Point	0.15	0.16	0.06	24
BD40	Davis Point	0.16	0.17	0.06	25
BD50	Napa River	0.16	0.16	0.06	24
BF10	Pacheco Creek	0.15	0.17	0.08	24
BF20	Grizzly Bay	0.13	0.14	0.06	25
BF40	Honker Bay	0.11	0.12	0.05	22
BG20	Sacramento River (near Mallard Island)	0.12	0.13	0.09	29
BG30	San Joaquin River (near Mallard Island)	0.14	0.16	0.09	28
BW10	Standish Dam	1.40	1.36	0.63	16
BW15	Guadalupe River	4.72	4.21	2.10	13
C-1-3	Sunnyvale	0.82	1.03	0.59	23
C-3-0	San Jose	0.91	0.86	0.33	23

Table A-3
Summary of total selenium concentrations in water for the period of 1993-2005 for the whole Bay
(data source: RMP).

Site Code	Site Name	Median (µg/L)	Mean (µg/L)	Standard Deviation	Count
BA10	Coyote Creek	0.39	0.47	0.25	17
BA20	South Bay	0.33	0.35	0.15	21
BA30	Dumbarton Bridge	0.26	0.28	0.12	29
BA40	Redwood Creek	0.19	0.20	0.06	20
BB15	San Bruno Shoal	0.16	0.17	0.08	19
BB30	Oyster Point	0.14	0.16	0.08	21
BB70	Alameda	0.16	0.19	0.16	19
BC10	Yerba Buena Island	0.12	0.16	0.09	23
BC20	Horseshoe Bay	0.11	0.17	0.12	19
BC30	Richardson Bay	0.11	0.13	0.08	22
BC41	Point Isabel	0.12	0.14	0.07	20
BC60	Red Rock	0.15	0.18	0.08	16
BD15	Petaluma River	0.25	0.24	0.09	19
BD20	San Pablo Bay	0.17	0.18	0.07	23
BD30	Pinole Point	0.17	0.18	0.08	23
BD40	Davis Point	0.18	0.21	0.08	23
BD50	Napa River	0.19	0.20	0.05	22
BF10	Pacheco Creek	0.19	0.19	0.07	22
BF20	Grizzly Bay	0.17	0.17	0.07	23
BF40	Honker Bay	0.15	0.16	0.05	22
BG20	Sacramento River (near Mallard Island)	0.13	0.15	0.08	27
BG30	San Joaquin River (near Mallard Island)	0.16	0.18	0.09	26
BW10	Standish Dam	1.70	1.65	0.82	14
BW15	Guadalupe River	5.59	4.76	2.58	12
C-1-3	Sunnyvale	1.02	1.14	0.58	23
C-3-0	San Jose	1.10	0.97	0.38	22

Table A-4
Summary of selenium concentrations in sediments for the period of 1993-2005 for the whole Bay
(data source: RMP)

Site code	Site Name	Median ($\mu\text{g/g}$)	Mean ($\mu\text{g/g}$)	Standard Deviation ($\mu\text{g/g}$)	Count
BA10	Coyote Creek	0.32	0.31	0.10	16
BA21	South Bay	0.34	0.44	0.25	16
BA30	Dumbarton Bridge	0.33	0.35	0.10	16
BA41	Redwood Creek	0.32	0.33	0.16	20
BB15	San Bruno Shoal	0.30	0.28	0.07	14
BB30	Oyster Point	0.29	0.33	0.13	16
BB70	Alameda	0.30	0.34	0.11	14
BC11	Yerba Buena Island	0.28	0.30	0.15	20
BC21	Horseshoe Bay	0.19	0.25	0.14	16
BC32	Richardson Bay	0.25	0.27	0.09	16
BC41	Point Isabel	0.30	0.33	0.09	16
BC60	Red Rock	0.07	0.11	0.11	13
BD15	Petaluma River	0.29	0.31	0.12	14
BD22	San Pablo Bay	0.32	0.41	0.32	18
BD31	Pinole Point	0.28	0.36	0.27	20
BD41	Davis Point	0.11	0.15	0.17	16
BD50	Napa River	0.38	0.52	0.47	18
BF10	Pacheco Creek	0.11	0.15	0.12	16
BF21	Grizzly Bay	0.33	0.50	0.68	20
BF40	Honker Bay	0.31	0.38	0.20	14
BG20	Sacramento River (near Mallard Island)	0.10	0.14	0.13	19
BG30	San Joaquin River (near Mallard Island)	0.30	0.29	0.16	20
BW10	Standish Dam	0.51	0.49	0.17	10
BW15	Guadalupe River	0.53	0.54	0.09	8
C-1-3	Sunnyvale	0.31	0.33	0.19	15
C-3-0	San Jose	0.33	0.33	0.11	15

**Table A-5
Detailed Information on Selenium from POTWs in North San Francisco Bay**

NPDES	Name	Ports	Flow (mgd)	Period	Count	Conc. (ug/L)	Period	Count	Load	Total	Note
CA0038768	American Canyon	E-001-S (M-001)	0.89	11/02-11/04	355	1.16	12/02-6/05	32	1.42		2 ports, both included in calculation
		E-003-R/S (M-003)	0.99	5/04-12/04	214	1.06	1/03-6/05	31	1.46	2.87	
CA0038091	Benicia	E-001	2.99	8/99-4/07	2830	0.85	10/99-4/07	98.00	3.50		
CA0037648	CCC	E-001	45.81	1/98-5/07	3126	0.34	1/98-3/07	99	21.79		Overflow occurred only once in 1998, not regular discharge, not included in load estimate
		OV-001 Overflow & Bypass	102.50	1/98-2/98	55						
CA0038628	Central Marin	E-001/M-001	11.00	5/98-3/07	3076	0.81	5/98-3/07	99	12.26		
CA0038547	Delta Diablo	E-001-D	11.46	1/99-4/07	2829	4.07	1/99-4/07	104	64.50		
CA0037702	EMUD	E-001	74.64	8/98-4/07	3194	0.34	9/98-4/07	294	34.76		
CA0038024	Fairfield-Suisun	E-001-A	16.95	4/99-5/07	2553	0.75	12/98-10/03	95	17.45		Concentrations not reported for E-001-S, E-002, E-003, E-004, used E-001-A conc.
		E-001-S	15.73	12/98-5/07	2675						Some flow record for 001-S are the same to 001-A, E001-S not used for final load calculation
		E-002	0.02	1/00-4/06	1396				0.02		Mostly 0
		E-003	0.01	1/00-4/06	1400				0.01		Mostly 0
		E-004	1.44	12/98-4/07	1583				1.48	18.97	
CA0037851	Las Gallinas	E-001 Dry (May)	3.20	5/03-5/06	50						Dry weather concentration not available
		E-001 Wet (Nov to Apr)	3.75	12/01-4/07	968	0.95	1/01-3/07	15	2.48		

NPDES	Name	Ports	Flow (mgd)	Period	Count	Conc. (ug/L)	Period	Count	Load	Total	Note
		E-002 Wet (Nov to Apr)	1.44	11/06-4/07	181				0.95	3.43	E-002 concentration not available
CA0037770	Mount View	E-001	1.98	6/99-4/07	2872	0.67	9/99-9/06	38	1.83		
CA0037575	Napa	E-001 Dry (May-October)	3.81	6/02-7/04	398	0.57	9/02-7/04	13	1.49		
		E-001 Wet (Nov - Apr)	13.98	1/99-5/04	573	0.27	1/99-5/04	26	2.60	4.10	
CA0037810	Petaluma	E-001 (Recycling)	4.01	5/02-03/07	773						Recycled water not discharging to the Bay, and not included in the load
		E-001	7.61	1/00-4/07	1377	0.65	1/99-4/07	119	6.88		
CA0037796	Pinole	E-001	3.18	1/00-5/07	2708	0.91	3/00-4/07	47	4.00		
CA0037826	Rodeo	E-001	0.80	3/00-4/07	2613	0.80	3/00-3/07	30	0.89		
CA0038067	Sausalito	E-001	1.63	12/99-4/07	2615	2.46	12/99-4/07	85	5.53		
CA0037800	Sonoma	E-001 (Recycling)	2.701	5/00-11/01	170						Concentration reported with high DL of 5 ug/L, load not calculated
		E-001	4.089	1/99-7/04	1287						
CA0110116	Treasure Island	E-001	0.534	10/00-4/07	2433	0.48	8/00-7/04	46	0.36		
CA0037699	Vallejo	E-001 Carquinez (deep)	13.17	1/99-4/07		0.96	5/00-4/07	79	17.47		EPA PCS database has E-001 and E-002; load is the sum of E-001 and E-002
		E-002 Mare (deep)	2.69	1/00-4/06	154	0.767	1/02-4/06	15	2.85	20.32	
		Mare (shallow)	7.38	1/99-1/99	5						Mare (shallow) only 5 records. Not included.
CA0038539	West County/Richmond	E-001 DC (Combined)	14.14	3/03-5/07	1520	1.727	2/02-4/07	60	33.74		Conc only reported for E-001-DC
		E-001 D1 (West County)	9.33	10/2-5/07	1672						Load is only calculated for E-001-DC

NPDES	Name	Ports	Flow (mgd)	Period	Count	Conc. (ug/L)	Period	Count	Load	Total	Note
		E-001 D2 (Richmond)	8.37	10/2-5/07	1642						
CA0037958	Novato SD	E-001 Ignacio Dry	4.01	5/99-5/99	31	0.475	5/99-3/04	4	2.63		
		E-001 Ignacio Wet	4.48	11/02-11/02	21						
		E-002 Novato Wet	2.23	5/99-11/04	119	0.833	11/02-3/04	4	2.57		
		E-003 Combined Dry	5.67	5/99-5/99	31						
CA0037711	Sewerage Agency of So. Marin	E-001	3.3	1/99-5/07	3043	1.394	1/99-4/07	133	6.36		
CA0037753	Marin Co. S.D. no. 5 (Triburon)	E-001	1.02	1/00-4/07	2250	1.93	1/00-4/07	47	2.72		
CA0037966	City of Calistoga	E-001 (Dry)	0.87	1/00-5/05	962	0.51	1/00-1/06	19	0.61		
		E-002 (Wet)	0.65		29						
CA0038016	City of Saint Helena	E-001	1.114	1/04-1/04	31	<0.5			0.38		Concentration taken from permit
		E-001S	1.452								
CA0037885	Contra Costa Co. S.D. No. 5 (Port Costa)		0.02			NA			NA		
CA0037427	Marin Co. S.D. no. 5 (Paradise Cove)		0.02			0.73			0.02		Concentration taken from permit

TECHNICAL MEMORANDUM 3: NORTH SAN FRANCISCO BAY SELENIUM TOXICOLOGICAL ASSESSMENT

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ABBREVIATIONS

AET	apparent effects threshold
ANOVA	Analysis of variance
CDH	California Department of Health
DFG	Department of Fish and Game
dw	dry weight
EC01	concentration at which an effect is observed in 1% of the population (i.e., effect concentration 1%)
EC10	concentration at which an effect is observed in 10% of the population (i.e., effect concentration 10%)
LC50	concentration lethal to 50% of test subjects
LOAEL	lowest observed adverse effects level
MBTA	Migratory Bird Treaty Act
Na ₂ SeO ₃	sodium selenite
NRC	National Research Council
NIWQP	National Irrigation Water Quality Control Program
NOAEL	no observed adverse effect level
Se	selenium
SeMet	selenomethionine
SFEI	San Francisco Estuary Institute
SMCV	Species mean chronic values are calculated by taking the geometric mean of the effect thresholds (e.g., NOAEL and LOAEL) for a particular species.
TMDL	total maximum daily load
UCL95	95% upper confidence limit on the mean
USDOI	U.S. Department of the Interior
USEPA	U.S. Environmental Protection Agency
USFWS	U.S. Fish and Wildlife Service

USGS U.S. Geological Survey
ww wet weight

1 INTRODUCTION

This technical memorandum provides a review of the available information on the toxicity of selenium to invertebrates, fish, birds, and marine mammals. This information has been developed to support the Regional Water Quality Control Board, San Francisco Bay Region (Water Board) in determining numeric targets for the selenium TMDL for the North San Francisco Bay (North Bay). The review of the selenium toxicity data was conducted in several steps. First, the available toxicity data from the published scientific literature and unpublished reports were compiled. These documents were identified from on-line searches of scientific references and the literature-cited sections of these reports were reviewed to identify unpublished reports. We estimate that greater than 95% of the relevant English-language literature has been reviewed. Next, the reported toxicity values were screened to identify those data that were most relevant to setting a numeric target for North Bay fish and wildlife. Screening criteria included:

- Chronic exposure to single chemical (selenium)
- Controlled experimental conditions
- Dietary exposure
- Tissue concentrations reported for exposed animals

The reported toxicity values (tissue concentrations) for individual species can exhibit a wide range due to differences in the corresponding toxicity endpoint of the test. Therefore, the test endpoint merits special attention in interpreting the reported toxicity values. The tables in this report, summarizing the selenium toxicity studies evaluated, report both the toxicity value and the test endpoint.

The focus of this report is on the compilation of relevant toxicity values. Some of the key issues to consider in interpreting the results of the laboratory tests and data analyses are also identified.

1.1 BACKGROUND INFORMATION

The current EPA and California state freshwater water chronic quality criterion for the protection of aquatic life (5 µg/L) has been criticized as inadequately representative of the toxic risks of selenium to aquatic life. Recent studies on selenium toxicity in aquatic food chains have generally reached the conclusion that a water-based criterion is not suitable due to "...temporal [and spatial] changes in concentrations, speciation, and rates of transfer between water, sediment and organisms..." (Hamilton 2004). Since the primary route of exposure to selenium is via the diet, and selenium is highly bioaccumulative, these differences can mean that a concentration of selenium in water that results in adverse effects in one location may not result in adverse effects to the same species in another location. Thus, the current recommendation (USEPA 2004, Chapman 2007, Hamilton 2002, 2004) for the appropriate media for regulation of selenium in the aquatic environment is not water, but rather tissue.

In 1987 in the North San Francisco Bay (hereinafter referred to as the “North Bay”), “...the California Department of Health (CDH) issued a health advisory for the consumption of three [sic] species of diving ducks in Suisun Bay, near San Francisco. These diving ducks (i.e., surf scoter, lesser and greater scaup) feed on bottom-dwelling animals (clams, mussels), which concentrate selenium from sediment and phytoplankton. In a study by the California Department of Fish and Game, the mean selenium levels in the muscle of duck were as follows: scoters, 3.6 ppm Se, wet weight; scaups, 2.2 ppm Se, wet weight. These levels were up to 5 times higher than mean Se levels in similar species in control areas (i.e., Humboldt Bay near the border of Oregon and California). The CDH recommended limiting the consumption of scoters to 4 oz/2 wk and of scaups to 4 oz/wk. Because of the known effects of selenium on the reproduction of birds, the CDH recommended that women of child-bearing age and children, 15 years old not consume these ducks” (Barceloux 1999).

In addition to the CDH health advisories for the consumption of diving ducks, the North Bay including Suisun Bay, Carquinez Strait, San Pablo Bay and Central Bay were listed in 1998, 2002, and 2006 under section 303(d) of the Clean Water Act due to impairments to both wildlife and human-health beneficial uses (Abu-Saba and Ogle 2002). It is on the basis of these listings that the Regional Water Quality Control Board, San Francisco Region (Water Board) is developing the Total Maximum Daily Load for the North Bay.

1.2 RELEVANT TOXICITY DATA

Several approaches have been used to develop screening values in the scientific and regulatory literature. These approaches include:

- LOAELs
- Effect thresholds
- Species mean chronic values
- EC01 or EC10
- Species sensitivity distributions

In the literature on selenium toxicity to fish, the approach that has generally been used is to set the screening value equal to the lowest LOAEL (i.e., the **lowest observed adverse effect level**) that has been reported (e.g., Hamilton 2003, 2004). When there is a large body of literature, with many reported LOAELs, this approach is likely to come close to the concentration at which effects first appear. However, when there are only a few studies, it is likely that effects begin at a level below the lowest LOAEL reported. For that reason, it may be advisable to use an SMCV, EC10, or effect threshold (see below) instead.

Effect thresholds are calculated as the geometric mean of the NOAEL (i.e., the highest **no observed adverse effect level**) and LOAEL reported for the same effect in an individual study. Since toxicity tests do not generally test many different concentrations, and effects may occur at concentrations below the LOAEL, calculating the geometric mean of the NOAEL and the LOAEL is one way to add a margin of safety to the LOAEL. That is,

effects are likely to occur somewhere between the NOAEL and the LOAEL. The USEPA (1985, 2003) has made the decision that the geometric mean of the NOAEL and LOAEL is representative of where those effects are likely to occur.

Species mean chronic values (SMCVs) are used by USEPA in the calculation of water quality criteria (USEPA 1985). An SMCV is calculated by taking the geometric mean of the effect thresholds for a particular species. When there is only one study available, the results of that study are regarded as the SMCV.

Another approach that can be used to find the concentration at which effects are likely to occur between the NOAEL and LOAEL is to pool the data from similar studies and perform a regression (e.g., biphasic, hockey-stick, or logistic) on the response data. The data is generally only from a single species. This approach has been used in State of Utah (Ohlendorf 2007) by pooling the data from 6 studies on mallards and performing regressions on the concentration of selenium in feed and eggs vs. reproductive success. The State of Utah derived an EC10 (i.e., the **effect concentration 10%** or the concentration at which an effect is observed in 10% of the population) for selenium in mallard diets and eggs protective of reproductive success. This same approach can also be used to calculate an EC01 (i.e., **effect concentration 1%**), which will be lower, but protective of a greater proportion of individuals.

Species sensitivity distributions are another approach that have been used to derive screening values. In this approach, the probability distribution of some measure of toxicity (e.g., NOAEL, LOAEL, effect threshold, SMCV, LC₅₀, etc.) for multiple animal species is calculated. From the probability distribution, a screening value is then calculated that is protective of a certain proportion of the species (e.g., 95%). USEPA calculates percentiles of species sensitivity distributions for use in the derivation of water quality criteria (Posthuma et al. 2002). This approach is similar to the EC10 approach described above, except that it always uses data from multiple species, with each data point representative of a single species, and uses probability distributions instead of regressions to derive screening values. For the recent acute criterion for copper, USEPA compared their calculated value to a species sensitivity distribution (Figure 1-1) and found that it was protective of 95% of the genera making up the acute copper toxicity database (USEPA 2007a). The species sensitive distribution (Figure 1-1) contains the genus mean acute value (GMAV) for 27 genera, including 15 species of invertebrates, 22 species of fish, and 1 amphibian species. Each GMAV was calculated as the arithmetic geometric mean of the species mean acute values (SMAV) for the species within that genera and the SMAV was calculated as the geometric mean of the individual value. The selected final acute value of 4.67 ug/L exceeds only one of 27 GMAVs (Figure 1-1); i.e., the GMAV for that cladoceran (an invertebrate) *Daphnia*.

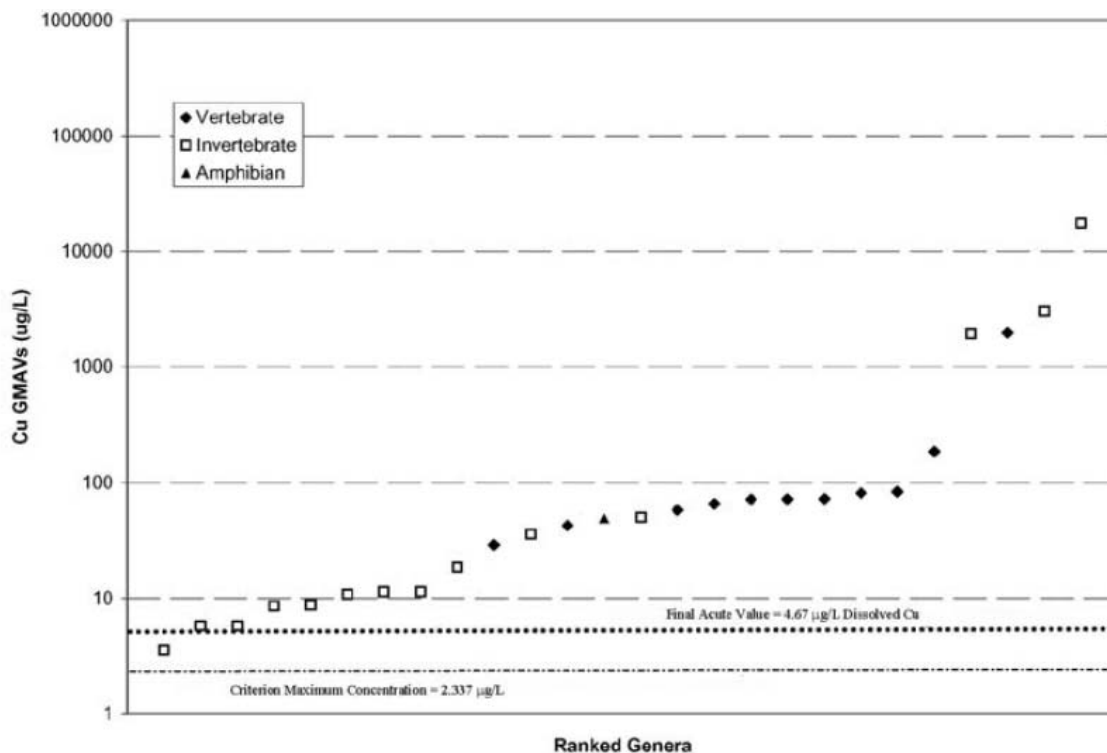


Figure 1-1 Ranked freshwater genus mean acute values (GMAVs) for copper (USEPA 2007a).

Effect thresholds and SMCVs will be calculated for the toxicity data presented in the following chapters. The lowest LOAEL will also be noted. Where an EC01, EC10, or species sensitivity distribution has been reported, that will also be noted. However, the calculation of these other measures of toxicity is not included in this review.

Selenium is an essential micro-nutrient. Adverse effects occur both when selenium concentrations are too low and too high in the diet (see Figure 1-2). At low concentrations, selenium is an essential micro-nutrient in animals. If the concentration of selenium in the diet is not adequate, selenium deficiency may result. The symptoms of selenium deficiency include edema, white muscle disease, reduced growth, reduced disease resistance, liver necrosis, morbidity, and increased mortality (National Research Council 1980, 2005, Ulrey 1992). At high concentrations, however, selenium can cause toxic effects, including emaciation, hair/feather loss, reduced reproductive success, reduced growth, developmental deformities, and mortality (National Research Council 1980, 2005, Ohlendorf 2003).

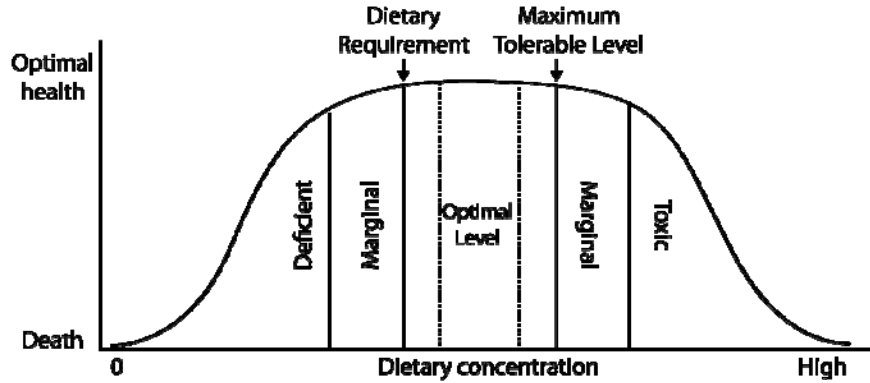


Figure 1-2 Health vs. dietary selenium concentration (adapted from NRC 2005).

The occurrence of effects in fish from low dietary selenium concentrations is seen in one of the toxicity studies examined in this report. In a study on fingerling channel catfish, Gatlin and Wilson (1984) were able to show that dietary selenium concentrations below approximately 0.3 mg/kg resulted in reduced weight gain. Above that, there was a plateau in the response (i.e., the optimal level) in which increased selenium concentrations did not have an adverse effect. However, the plateau ends at approximately 10 mg/kg, with concentrations above that also resulting in reduced weight gain (Figure 1-3). This has also been observed for calcium, magnesium, manganese, molybdenum, phosphorus, potassium, sodium, sulfur, and zinc (NRC 2005).

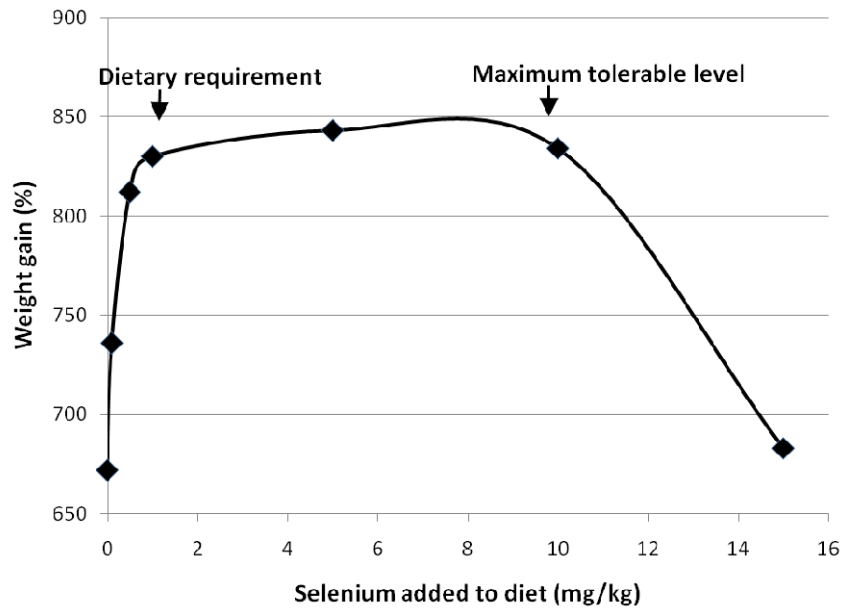


Figure 1-3 Weight gain in fingerling channel catfish as a function of dietary selenium (Gatlin and Wilson 1984).

Thus, screening values for dietary selenium concentrations should be set above the dietary requirement. When dietary concentrations are below the dietary requirements, adverse effects could theoretically occur from deficiency. Further, when dietary concentrations are near the requirements, a proportion of the population may also be adversely affected by selenium deficiency. In turn, these effects could lead to the very reduction in fish and bird

populations that the selenium TMDL sought to avoid by reducing selenium concentrations. The dietary requirements of fish, birds, pigs, and other mammals have been determined by the NRC (1993, 1994, 1998) and will be presented in each of the sections evaluating the toxicity to the biota of the North Bay.

2 INVERTEBRATE TOXICITY REVIEW

Invertebrates are an integral part of many food chains in the North Bay, supporting many species of fish and birds, including species of recreational interest as well as threatened and endangered species. This suggests that if selenium negatively impacts the aquatic invertebrates in the North Bay, the result may be reduced food availability for the fishes and birds of the North Bay. Ultimately, this may lead to a reduction in the population sizes of those fishes and birds, even in the absence of direct impacts to the fishes and birds themselves from selenium. This suggests that the potential impacts of selenium on aquatic invertebrates in the North Bay should be part of the TMDL process.

While there is a large amount of literature on the toxicity of selenium to fishes, birds, and mammals, the chronic toxicity literature is very sparse for aquatic invertebrates. Thus, there is very little literature that may help the Water Board to determine whether the aquatic invertebrates in the North Bay are impacted by selenium. Similarly, the paucity of information on the toxicity of selenium to aquatic invertebrates means that there are very few published sources of selenium screening values; e.g., no “Consensus-Based Sediment Quality Guidelines” (MacDonald et al. 2000), no California sediment quality objectives (SWRCB 2007), and only an apparent effect threshold in the NOAA SQUIRTs (Buchman 1999).

Despite the paucity of selenium toxicity data for aquatic invertebrates, there are a few chronic toxicity studies that may be informative to the Water Board. These studies are listed and briefly described below:

- Alaimo et al. (1994)
- Bielmeyer et al. (2005)
- Brasher and Ogle (1993)
- Debruyn and Chapman (2007)
- Hyne et al. (2002)
- Ingersoll et al. (1990)
- Jensen et al (2007)
- Malchow et al (1995)
- Naddy et al (1995)
- NOAA SQUIRTs (Buchman 1999)

Alaimo et al. (1994)

The authors performed chronic toxicity in a laboratory on the larvae of the midge *Chironomus decorus*. Chironomids are a major component of fish and waterfowl diet.

Midge eggs were placed in “moderately hard” water and, after hatching, were fed with powdered plants that were collected from evaporation ponds in California with varying concentrations of selenium. The authors found that increased selenium concentrations in the powdered food resulted in lower body weights of the growing midges with a NOAEL and LOAEL of approximately 0.5 and 1.6 mg/kg-dw, respectively, in the powdered food (effect threshold of 0.9 mg/kg-dw); the NOAEL and LOAEL for selenium in midge tissues were both below the detection limit of approximately 0.5 mg/kg-dw. In this experiment, selenium was only added via the food, but that also led to increases in selenium in the water column over time.

Bielmeyer et al. (2005)

The authors performed chronic toxicity tests in a laboratory on the larvae of sea urchins. Although the species tested, *Diadema antillarum*, does not occur in the North Bay, the authors state that “sea urchin larvae have been shown to be highly sensitive to metals and therefore have been extensively used in marine pollution bioassays” (Bielmeyer et al. 2005). Therefore, their results should be applicable to the North Bay in a general sense. The authors examined the development of larval sea urchins by exposing them to 0, 5, 10, 20, 36, 73 µg/L selenium as Na₂SeO₄ for 40 hours in sea water. The authors found that selenium caused abnormal development with an EC₅₀ of 26 µg/L. However, there were no apparent adverse effects at up to 20 µg/L (i.e., the NOAEL was 20 µg/L). The experiment design that the authors used did not expose the parents to selenium, but only the larvae. In the North Bay, both the parents and the offspring will be exposed, which may potentially increase selenium sensitivity.

Brasher and Ogle (1993)

The authors performed chronic toxicity tests in a laboratory on the freshwater amphipod *Hyallela azteca*. Separate experiments were conducted using sodium selenite at 0, 50, 100, 200, 300, and 400 µg/L and sodium selenate at 0, 100, 250, 350, 500, and 700 µg/L for 24 days. Reproduction was reduced at 200 µg/L selenite but no effects were observed for selenate.

Debruyn and Chapman (2007)

The authors compiled existing toxicity data on major effects (i.e., toxic effects that are likely to affect a species at the population level, including reproduction and growth) that included water, dietary, or tissue selenium concentrations associated with toxic effects to 29 macroinvertebrate species. Studies reporting dietary and tissue concentrations were pooled across freshwater benthic, freshwater planktonic, and terrestrial invertebrate groups. For chronic waterborne exposures, the authors found that the amphipod *Hyallela* was the most sensitive with a median lethality reported at 100 µg/L selenite, 200 µg/L selenate, and a >50% reduction in reproduction at 100 µg Se/L selenate. Sublethal effects from dietary exposures were found to range from 1 to 80 mg/kg-dw. Sublethal effects for tissue concentrations of selenium were found to range from 1 to 30 mg/kg-dw. Although the authors used the data collected to construct a percentile based species sensitivity distribution (not a probability), they did not use the distributions to calculate values protective of a percentage of the species observed.

Hyne et al. (2002)

The authors performed chronic toxicity tests in a laboratory on juveniles and adults of the estuarine amphipod *Corophium* sp. Amphipods exposed to sediments spiked with seleno-L-methionine to give final concentrations of 0, 0.3, 1, 3, and 10 mg/kg-dw. Selenium was not added to either the water or the food given to the amphipods and all experiments were conducted using seawater. The only response measured in the amphipods was mortality. The results of these experiments are summarized in the Table 2-1 below (from Hyne et al. 2002).

Table 2-1
Summary of Results from Hyne et al. (2002)

Lifestage	Test conditions of overlying water	10-day LC ₅₀ sediment (dry wt) µg Se/g (95% CL)	10-day NOAEL sediment µg Se/g (dry wt)	10-day LOAEL sediment µg Se/g (dry wt)
Juvenile	No renewal	1.6 (1.3-1.9)	0.84	2.0
Juvenile	Daily renewal	6.3 (5.5-7.2)	1.7	5.0
Adult	No renewal	7.6 (6.8-8.4)	4.6	11.0

These results indicate that significant mortality was observed at concentrations as low as approximately 2 mg/kg-dw. An effect threshold was calculated for juvenile mortality in waters without renewal of 1.3 mg/kg-dw. However, it should be noted that since the authors only measured mortality, sublethal effects may be expected at lower sediment concentrations.

Ingersoll et al. (1990)

The authors performed chronic toxicity tests in a laboratory on the freshwater arthropods *Daphnia magna* and *Chironomus riparius*. Chironomids are a major component of fish and waterfowl diet. The experiments produced LOAELs for inorganic selenium in waterborne exposures of 85 µg/L for *Daphnia* and 837 µg/L for *Chironomus*.

Jensen et al. (2007)

The authors performed freshwater chronic toxicity tests in a laboratory on the larvae of the southern house mosquito *Culex quinquefasciatus*. *Culex* spp. are algal and bacterial feeders and are important as food for many organisms. The larvae were exposed to 2, 4, 8, 16, and 32 mg/L selenate. The experiments produced a LOAEL for reduced growth of 2 mg/L.

Malchow et al. (1995)

The authors performed freshwater acute toxicity tests in a laboratory on the larvae of the midge *Chironomus decorus*. Chironomids are a major component of fish and waterfowl diet. The experiments consisted of feeding the midge larvae with a diet of algae (*Selenastrum capricornutum*) cultured in three concentrations of selenite (0, 10, and 40 µg/L) or four concentrations of selenate (0, 4, 10, and 40 µg/L). The experiments produced a NOAEL and LOAEL for reduced body weight of 1.10 and 2.11 mg/kg-dw, respectively, in algae (effect threshold of 1.5 mg/kg-dw); or a NOAEL and LOAEL of <0.25 and 2.55 mg/kg-dw, respectively, in the midges (effect threshold of 0.8 mg/kg-dw, assuming the NOAEL was 0.25). Although this was an acute toxicity test, this is one of the few studies where invertebrates were exposed to selenium in the diet. Chronic tests may result in toxicity observed at lower concentrations.

Naddy et al (1995)

The authors performed freshwater chronic (90 day) toxicity tests in a laboratory using *Ceriodaphnia dubia*. The daphnia were exposed to <170, 510, 610, and 870 µg/L selenate. No effects on survival or reproduction were observed at any concentration.

NOAA SQuiRTs (Buchman 1999)

The National Oceanic and Atmospheric Administration has published a set of screening values called the Screening Quick Reference Tables (SQuiRTs). The SQuiRTs contain a marine sediment apparent effects threshold (AET) protective of amphipods of 1 mg/kg-dw. AETs are described as "...the concentration above which adverse biological impacts would always be expected... Conversely, adverse impacts are known to occur at levels below the AET... AET values were developed for use in Puget Sound (Washington)..."

2.1 DISCUSSION

"Selenium toxicity is greater in laboratory tests in which organisms are fed than in water only tests, because food accumulates Se from the aqueous phase, adding substantially to the test organism's total exposure" (Debruyne and Chapman 2007). Therefore, the results of water only tests can result in apparently high toxicity thresholds for invertebrates; e.g., 26 µg/L for sea urchins (Biemeyer et al. 2005) and 2,000 µg/L for *Culex quinquefasciatus* (Jensen et al. 2007). Similarly, for sediment dwelling invertebrates, exposures to selenium in sediments appears to result in adverse effects at relatively low levels.

From the few studies presented above that have been performed using either dietary or sediment exposures, the following Table 2-2 was constructed:

Table 2-2
Effect thresholds for invertebrates exposed to dietary or sediment-bound selenium

Organism	Exposure route	Effect Threshold (mg/kg-dw)			Reference
		Diet	Sediment	Organism	
midge	diet	0.9	-	<0.5	Alaimo et al. (1995)
amphipod	sediment	-	1.3	-	Hyne et al. (2002)
midge	diet	1.5	-	0.8	Malchow et al. (1995)

These data indicate that invertebrates may be affected by relatively low selenium concentrations, when exposed to selenium in dietary items or in sediments (for sediment dwelling biota).

Nutritional requirements

Selenium is a micro-nutrient (see Section 1). When animals do not have enough selenium in their diet, selenium deficiency results (NRC 1993, 1994). While the NRC (1993, 1994, 1998) has not established selenium nutritional requirements for invertebrates, it has established nutritional requirements for animals that potentially feed on invertebrates: 0.25-0.3 mg/kg for fish (NRC 1993), 0.17-0.33 for pigs (NRC 1998), and 0.16-0.22 mg/kg for birds (NRC 1994).

2.2 CONCLUSIONS

The effect thresholds shown in the table above are similar to the few published lower bound values available; i.e., the AET for selenium in marine sediments of 1 mg/kg is very close to

the effect threshold of 1.3 mg/kg-dw observed by Hyne et al. (2002); and the lower bound dietary and organism selenium concentrations published by Debruyn and Chapman (2007) of 1 mg/kg-dw each are close to the effect thresholds reported for mussels above (0.9-1.5 mg/kg-dw for diet and <0.5-0.8 mg/kg-dw for organism). All of these values are above the dietary requirements for fish, birds, and pigs (NRC 1993, 1994, 1998), although some are close.

Based upon the data presented here, there are several options for screening values protective of invertebrates. Those options are as follows (all in units of mg/kg-dw):

1. Dietary items
 - a. Lowest effect threshold: 0.9
 - b. Lowest LOAEL: 1.6
2. Sediment
 - a. Lowest effect threshold: 1.3
 - b. Lowest LOAEL: 2.0
 - c. AET: 1.0
3. Organism (excluding non-detects)
 - a. Lowest effect threshold: 0.8
 - b. Lowest LOAEL: 2.55

3 FISH TOXICITY REVIEW

The North Bay supports a diverse fish biota. The fish supported include both sportfish and threatened and endangered fish species. The five most common sportfish in the North Bay are (SFEI 2000; listed in order catch frequency):

1. Striped bass (*Morone saxatilis*)
2. Halibut (*Paralichthys californicus*)
3. Jacksmelt (*Atherinopsis californiensis*)
4. White sturgeon (*Acipenser transmontanus*)
5. White croaker (*Genyonemus lineatus*)

In addition to the sportfish listed above, the North Bay supports the following threatened and endangered fishes (USFWS 2007):

1. Chinook salmon (*Oncorhynchus tshawytscha*)
2. Delta smelt (*Hypomesus transpacificus*)
3. Green sturgeon (*Acipenser medirostris*)
4. Longfin smelt (*Spirinchus thaleichthys*)
5. Sacramento perch (*Archoplites interruptus*)
6. Sacramento splittail (*Pogonichthys macrolepidotus*)
7. Steelhead trout (*Oncorhynchus mykiss*)
8. Tidewater goby (*Eucyclogobius newberryi*)

Selenium in the North Bay may adversely impact these fish by causing reduced production of viable eggs, post-hatch mortality, deformities in growing larvae, and various pathological effects in the kidneys, liver, heart, and ovaries (Hamilton 2003, 2004; Lemly 2002a). These identified effects may lead to population declines of both the sportfish and the threatened and endangered fishes in the North Bay. Therefore, as part of the selenium TMDL for the North Bay, selenium screening values will be developed that are protective of the species listed above.

As stated in the Introduction (see Section 1), the potential screening values that are proposed here are tissue concentrations. For fish, measuring the concentration of selenium in dietary items poses a logistical challenge. Mainly, the challenge lies in that many fish feed on a wide array of small prey items. Collecting the right kind of prey items, and a sufficient number for analysis, can be very time consuming. Instead, it is generally recommended that selenium be measured in the fish of concern (Hamilton 2002, 2003, 2004, USEPA 2004). Additionally, it is recommended that these measurements be made in whole fish due to "...practical reasons of sampling and because a sufficient data base containing chronic effects based on whole-body tissue is present in the literature" (USEPA 2004). The amount of data for chronic effects based on other tissue types (e. g., ovary, liver, kidney, and muscle) is not as extensive and, therefore, not amenable to deriving screening values. Further, although "ovaries may be the best tissue to link selenium to reproductive effects..."

ovarian tissue is also only available seasonally and sometimes difficult to extract in quantities sufficient for analysis...” (USEPA 2004). Therefore, whole body concentrations in fish are recommended for use as screening values.

3.1 METHODS

Selenium toxicity data for the fishes that occur in the North Bay would be the most relevant for developing selenium fish tissue screening values for the North Bay. However, for the fishes in the North Bay, there is very limited toxicity data and almost no toxicity data for fishes at all in the salinity range that occurs in the North Bay; i.e., 1 to 33.5 ppt. Therefore, this review is largely limited to the evaluation of the freshwater toxicity literature.

Selenium toxicity studies on fishes were gathered from the scientific literature, as well as reports and other “grey literature.” The studies collected were evaluated to select those that provided fish tissue concentrations at which toxic effects from chronic selenium exposures were observed. To ensure that screening values were not influenced by other variables (e.g., other contaminants), only studies with controlled experimental designs were selected.

The criteria used to identify studies with usable toxicity information are as follows:

- A. provide a NOAEL and/or a LOAEL
- B. chronic
- C. exposed to selenium only
- D. only treatment was selenium exposure level
- E. contained tissue data
- F. fish (and their food) were raised in the laboratory under controlled conditions
- G. used a dietary exposure scenario; mesocosm experiments in which selenium was added to the water column meet this requirement

All studies that were reviewed are listed in Table 3-1. Studies that were determined to be unsuitable are noted in Table 3-1 using the designations from the list above.

Table 3-1
Selenium toxicity studies evaluated in this review. Studies that were excluded from review are indicated (see text above for an explanation of the criteria).

Study	Reference	Evaluation criteria failed	Study	Reference	Evaluation criteria failed
1	Bennett et al. (1986)	A	41	Hilton and Hodson (1983)	
2	Bertram and Brooks (1986)	A	42	Hodson et al. (1980)	E
3	Brandão et al. (1992)	A	43	Hodson et al. (1986)	A
4	Chapman (1992)	B	44	Holm et al. (2005)	F
5	Cleveland et al. (1993)		45	Hunn et al (1987)	G
6	Coughlan and Velte (1989)	F	46	Kennedy et al. (2000)	F
7	Coyle et al. (1993)		47	Kimball (1978)	E
8	de Rosemond et al. (2005)	A	48	Klaverkamp et al. (1983)	E
9	Dobbs et al. (1996)		49	Kleinow (1984)	A
10	Doroshov et al. (1992)		50	Kleinow and Brooks (1986a)	A
11	Finger and Bulak (1988)	C,D	51	Kleinow and Brooks (1986b)	A
12	Finley (1985)	F	52	Lawler et al. (1981)	E
13	Gatlin and Wilson (1984)		53	Lemly (1993a)	
14	Gillespie and Baumann (1986)	F	54	Lemly (1993b)	F
15	Gissel-Nielsen and Gissel-Nielsen (1978)	E	55	Linville (2006)	
16	Goettl and Davies (1977)	E	56	Mehrle et al. (1982)	C,D
17	Goettl and Davies (1978)	E	57	Muscatello et al. (2006)	F
18	Hall et al. (1984)	C	58	Ogle and Knight (1989)	
19	Hall et al. (1985)	B,C,D	59	Pyron and Beitinger (1989)	A
20	Hall et al. (1987)	B,C,D	60	Saiki et al. (1992)	E
21	Halter et al. (1980)	B	61	Saiki et al. (2004)	C
22	Hamilton et al. (1986)	C	62	Schultz and Hermanutz (1990)	
23	Hamilton et al. (1990)		63	Schlenk et al. (2003)	B
24	Hamilton and Wiedmeyer (1990)	C	64	Sorensen and Bauer (1983)	E
25	Hamilton et al. (2000)	C	65	Sorensen and Bauer (1984)	A
26	Hamilton et al. (2002a)	C	66	Sorensen et al. (1982a)	A,E
27	Hamilton et al. (2002b)	C,D	67	Sorensen et al. (1982b)	A
28	Hamilton et al. (2005a)	C,D	68	Sorensen et al. (1983)	A
29	Hamilton et al. (2005b)	C	69	Sorensen et al. (1984)	F
30	Hamilton et al. (2005c)	C	70	Sorensen (1988)	F
31	Hamilton et al. (2005d)	C	71	Tashjian et al. (2006)	
32	Harrison et al. (1990)	A	72	Tashjian et al. (2007)	E
33	Hardy (2003)	F	73	Teh et al. (2002)	B,E
34	Hartwell et al. (1987a)	A	74	Teh et al. (2004)	
35	Hartwell et al. (1987b)	A	75	Vidal et al (2005)	
36	Hermanutz (1992)	E	76	Watenpaugh and Beitinger (1985a)	A
37	Hermanutz et al. (1992)		77	Watenpaugh and Beitinger (1985b)	B
38	Hicks et al (1984)		78	Watenpaugh and Beitinger (1985c)	A
39	Hilton et al. (1980)		79	Wooock et al. (1987)	E
40	Hilton et al. (1982)	A	80	Wise et al. (1993)	E

The reported effects from each study were grouped into one of two categories: major and minor effects. Major effects are those that have the potential to impact fish at the organism and/or population level (e.g., increased mortality, reduced fecundity, reduced growth, etc.). Minor effects are those that are measurable, but are unlikely to result in population level effects and/or the long-term impacts on individual fish performance was unclear (e.g., a change in an enzyme concentration). Where both major and minor effects were observed at the same concentration, the effects was assumed to be major. Only major effects were considered in development of screening values.

Effect thresholds were calculated as the geometric mean of the NOAEL and LOAEL reported for the same effect in an individual study, as is recommended in USEPA water quality criteria development guidance (USEPA 1985). Additionally, species mean chronic values (SMCVs) were calculated as the geometric mean of the effect thresholds (USEPA 1985). Studies that did not report a NOAEL were excluded from the calculation of an effect threshold and the SMCV. Note that excluding studies in which a NOAEL was not reported from the calculation of the SMCV results in lower SMCVs. USEPA (1985) provides the following rationale for the use of geometric means to calculate SMCVs:

“Geometric means rather than arithmetic means are used here because the distributions of individual organisms’ sensitivities in toxicity tests on most materials, ... are more likely to be lognormal than normal.”

The calculated SMCVs can then be used to evaluate the relative sensitivity of each species of fish to selenium and help determine the appropriate threshold for use.

In studies where selenium was not measured in whole fish (e.g., selenium was measured in liver or muscle), measured concentrations were converted to whole body concentrations using the equations presented by USEPA (2004). Additionally, tissue values based upon wet-weight values were converted to dry-weight values using either the %moisture values presented in the same study or default values from USEPA (2004). All conversion methods are described in detail in Appendix A.

3.2 RESULTS

The toxicity studies from Table 3-1 that were included in the evaluations below included 18 studies on the following fish species:

- Bluegill
- Channel catfish
- Chinook salmon
- Fathead minnows
- Rainbow trout
- Sacramento splittail
- White sturgeon

Bluegill

Five suitable studies were found on bluegills. Whole body effect thresholds ranged from 3.0 to 13.8 mg/kg-dw (Table 3-3).

Channel catfish

Two suitable studies were identified; i.e., Doroshov et al. (1992) and Gatlin and Wilson (1984). In the study by Doroshov et al. (1992), the exposure route was intramuscular

injection of selenomethionine. The degree of correlation between intramuscular injection and dietary exposures for selenium is unknown. In the study by Gatlin and Wilson (1984), selenium exposure was dietary. From these studies, we calculated whole body effect thresholds of 2.7 and 3.3 mg/kg-dw, respectively (Table 3-3).

Chinook salmon

A single suitable study was identified (Hamilton et al. 1990). That study evaluated selenium toxicity in both brackish and freshwaters, the whole body effect thresholds calculated from this study were 7.6 mg/kg-dw for freshwater and 17.1 mg/kg-dw for brackish water (Table 3-3) for fishes fed SeMet. These results indicate that selenium may be less toxic to salmon in brackish than in fresh waters.

Beckon (2007) also analyzed the data from Hamilton et al. (1990) but included the data from salmon that were fed field-collected mosquitofish. In our analyses, we excluded the data from salmon fed mosquitofish caught in the field as this exposed the salmon to multiple contaminants simultaneously which might have negatively influenced survival. Instead of calculating an effect threshold from the LOEL and NOEL from Hamilton et al. (1990), Beckon (2007) performed a regression of selenium concentration vs. survival and estimated an EC10 and EC20 of 1.84 and 2.5 mg/kg-dw, respectively. The analysis is shown in the figure below.

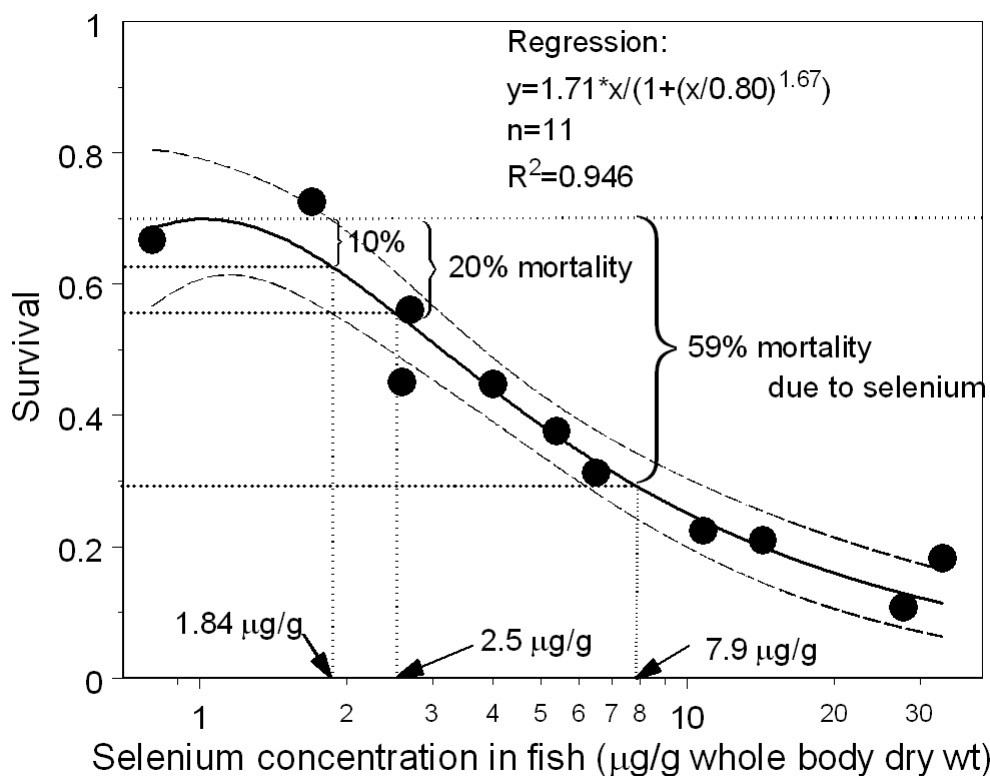


Figure 3-1 Biphasic regression analysis of the data from Hamilton et al. (1990)

It should be noted that performing a regression on the treatment means, instead of the raw data from individual test organisms, masks the true variation as associated with the experimental data; i.e., the confidence limits associated with the regression line in Figure 3-

1 could be much larger. Further, the nature of the relationship between fish survival and whole-body selenium concentrations (i.e., the EC10) may change when using the raw data. To examine the effects of using the data for the individual test organisms in the analysis, we used the treatment means and standard errors for the same 11 treatments that Beckon (2007) used to create the regression analysis in Figure 3-1 and repeated the experiment 10 times in a Monte Carlo simulation analysis. Assuming a normal distribution, we generated 2 data points per treatment (i.e., the number of data points collected by Hamilton et al. (1990)) and performed the same regression analysis. An example graph from one of the simulation experiments is provided in Figure 3-2.

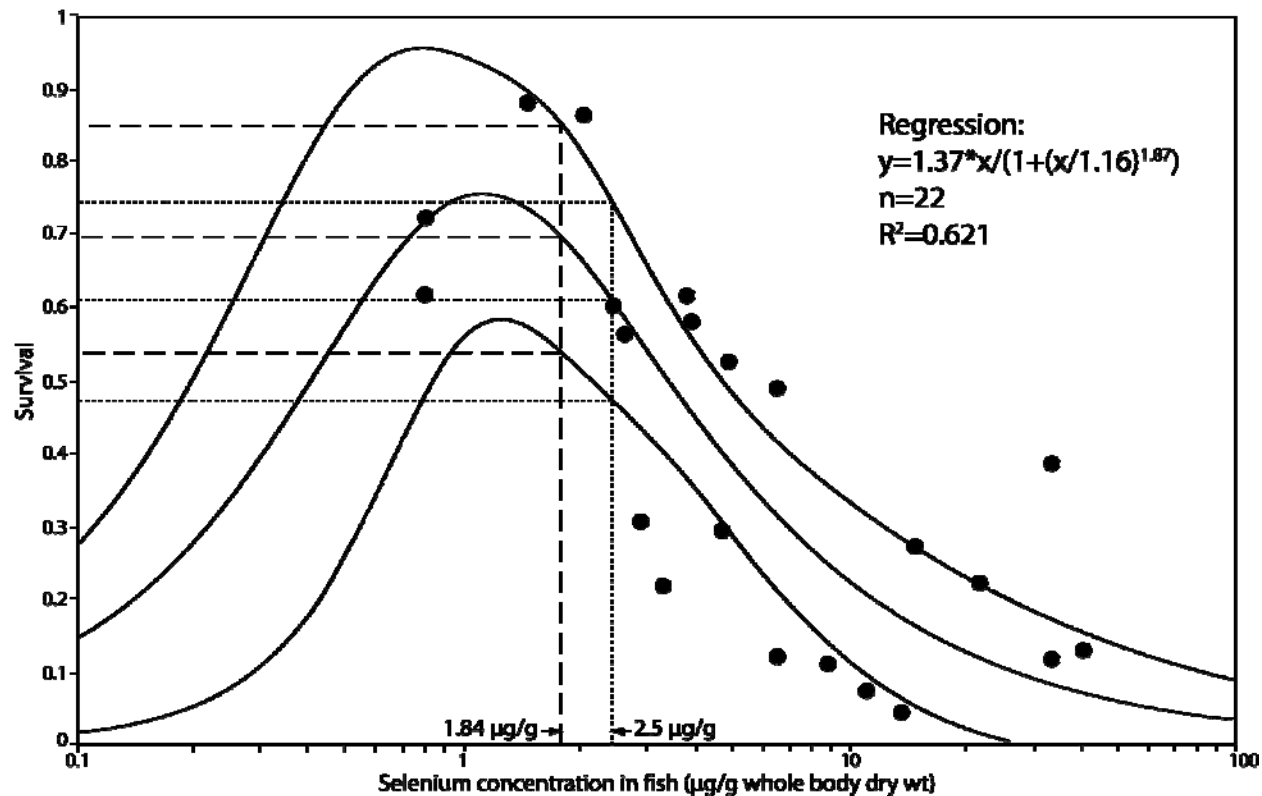


Figure 3-2 Biphasic regression based on simulated data from Hamilton et al. (1990)

From this simulated data set (Figure 3-2), it can be seen that performing a regression analysis on the (simulated) raw data (vs. the treatment means) leads to wider confidence intervals on the regression line. For example, the confidence limits on the regression line at the lowest treatment level are approximately 48-97% survival, as opposed to the approximately 57-80% survival that was calculated using only the treatment means.

The EC10 and EC20 derived from all 10 simulated experiments are presented in Table 3-2. The graphically derived confidence limits are also presented.

Table 3-2
The EC10 and EC20 from 10 simulated experiments and 95% confidence limits (CLs) on salmon survival at the EC10 and EC20

EC10			EC20		
(mg/kg-dw)	LCL for salmon survival at EC10 ^a	UCL for salmon survival at EC10 ^a	(mg/kg-dw)	LCL for salmon survival at EC20 ^a	UCL for salmon survival at EC20 ^a
1.91	52	83	2.47	47	73
2.03	55	88	2.61	49	79
1.59	57	76	2.38	50	68
1.82	51	74	2.50	46	70
1.60	47	72	2.26	41	64
1.88	46	71	2.52	41	64
1.82	50	77	2.46	45	68
1.94	48	75	2.74	43	67
2.42	55	72	3.33	49	64
1.85	49	74	2.65	44	66

Notes:

a - Confidence limits are graphically derived

UCL – upper confidence limit

LCL – lower confidence limit

Further, from Figure 3-2 and Table 3-2, it appears that the EC10 and the EC20 derived by Beckon (2007) may not significantly differ from each other and that both may not significantly differ from the no effect level in the regression; i.e., 70% survival. Testing for significant differences among the no effect level, the EC10, and the EC20 requires the ability to set 95% confidence limits. For non-linear regression analyses, the likelihood-ratio method is recommended for calculating confidence limits (see Moerbeek et al. 2004, Sand et al. 2006). However, we have not yet taken this next step to calculate confidence limits on the EC10 and EC20.

Fathead minnows

Three suitable studies were identified for fathead minnows. Whole body effect thresholds ranged from 6.0 to 73 mg/kg-dw (Table 3-3).

Rainbow trout

Four suitable studies were identified for rainbow trout (Table 3-3). Whole body effect thresholds for selenium ranged from 1.7 to 53.1 mg/kg-dw (Table 3-3). Using the treatment means from one of the suitable studies (i.e., Hilton et al. 1980; see study 38 in Table 3-3) Beckon (2007) derived an EC20 for juvenile rainbow trout of 2.15 mg/kg-dw based on a 20% reduction in body weight. However, this approach is subject to the same limitations discussed above for chinook salmon.

It should also be noted that Beckon (2007) used the raw data from a study that did not meet our selection criteria (i.e., Holm et al. 2005) to derive an EC20 of 2.93 mg/kg-dw for adult rainbow trout, based on a 20% reduction in the survival of fry from trout exposed to selenium.

Sacramento splittail

A single suitable study was identified (Teh et al. 2004). In that study, an effect threshold of 12.3 mg/kg-dw (muscle) was determined. Using the equations in USEPA (2004) to convert

muscle concentrations to whole body concentrations, an effect threshold of 10.8 mg/kg-dw (whole body) was calculated (Table 3-3).

White sturgeon

Two suitable studies were identified which evaluated the toxicity of selenium to white sturgeon (i.e., Linville 2006, Tashjian et al. 2006). Linville (2006) performed two sets of experiments: 1) injecting selenium into sturgeon eggs and 2) exposing adult sturgeon to dietary selenium. Only the results from the dietary exposure experiment are used in the evaluations presented here. We calculated whole body effect thresholds of 6.2 mg/kg-dw from Linville (2006) and 18.2 mg/kg-dw from Tashjian et al. (2006) (Table 3-3). William Beckon (2008) of the USFWS analyzed the data in Linville (2006) and derived an EC10 for selenium in muscle tissue which he then converted to a whole body concentration of 7.50 mg/kg-dw using a linear regression relating the two tissue types. The regression that Beckon (2008) used to convert selenium muscle concentrations to whole body concentrations was derived from the treatment means in Tashjian et al. (2006). Tetra Tech obtained the raw data from Tashjian et al. (2006) and used that to derive a linear regression relating muscle to whole body concentrations (see Appendix A). Using that regression, Tetra Tech converted the muscle tissue EC10 derived by Beckon (2008) into a whole body concentration of 11.9 mg/kg-dw. However, it should be noted that there were few data points available for the calculation of the EC10, making this value somewhat uncertain. The regression derived from the raw data from Tashjian et al. (2006) was also used to convert Linville's (2006) muscle NOAEL and LOAEL into whole body concentrations (Table 3-3).

Table 3-3
Summary of selenium toxicity studies evaluated in this review.

Fish	Study	Water Type	Life stage	Liver ¹		Muscle ¹		Whole Body		Effect Threshold (mg/kg-dw)			Endpoint
				NOAEL (mg/kg-dw)	LOAEL (mg/kg-dw)	NOAEL (mg/kg-dw)	LOAEL (mg/kg-dw)	NOAEL (mg/kg-dw)	LOAEL (mg/kg-dw)	Liver	Muscle	Whole Body	
bluegill	5	fresh	Juvenile	16.8	24.5	5.1	8.4	4.7	7.6	20.3	6.5	6.0	BW, L
bluegill	7	fresh	Adult	30.1	49.1	11.1	21.5	10.0	19.0	38.4	15.4	13.8	R
bluegill	10	fresh	Adult	12.3	26.0	5.8	10.4	5.5	9.3	17.9	7.8	7.1	D
bluegill	37	fresh	Adult	6.0	37.2	1.2	7.2	1.3	6.7	14.9	2.9	3.0	BW, R, S
bluegill	53	fresh	Juvenile	6.3	19.9	1.4	6.3	1.3	7.8	11.2	2.9	3.2	S, BW, L
channel catfish	10	fresh	Adult	7.3	12.5	2.1	3.8	2.0	3.6	9.6	2.8	2.7	S
channel catfish	13	fresh	Fingerling	-	-	3.0	3.5	3.1	3.5	-	3.3	3.3	BW
chinook salmon	23	fresh	Larvae ²	18.8	31.9	5.9	12.0	5.4	10.8	24.5	8.4	7.6	BW, L
chinook salmon	23	brackish	Juvenile ²	35.9	57.2	14.1	26.4	12.6	23.2	45.3	19.3	17.1	BW, L, S
fathead minnow	9	fresh	Larvae	-	121.0	-	72.8	-	62.0	-	-	-	BW
fathead minnow	58	fresh	Juvenile	18.8	21.9	5.7	6.6	5.4	6.6	20.3	6.1	6.0	BW
fathead minnow	62	fresh	Egg	-	-	-	-	1.6	19.6	-	-	5.5	D
rainbow trout	75	fresh	Larvae	6.1	9.9	1.3	2.5	1.2	2.3	7.8	1.8	1.7	BW, L
rainbow trout	38	fresh	Juvenile	153.2	197.2	-	-	46.8	60.3	173.8	-	53.1	BW, FG, S
rainbow trout	39	fresh	Juvenile	42.0	95.0	-	-	12.6	28.9	63.2	-	19.1	BW, S, FG
rainbow trout	41	fresh	Juvenile ³	21.0	71.7	1.0	4.3	1.0	4.0	38.8	2.1	2.0	BW, FG
Sacramento splittail	74	fresh	Juvenile	23.0	26.8	10.1	15.1	9.0	12.9	24.8	12.3	10.8	D
white sturgeon	55	fresh	Adult	1.4	10.4	1.3	12.1	3.1	12.3	3.9	4.0	6.2	D
white sturgeon	71	fresh	Juvenile	22.0	37.4	22.9	36.8	14.7	22.5	28.7	29.0	18.2	BW, SA

Notes:

1 - shaded cells represent concentrations predicted from measurements in other tissues (see Appendix A)

2 - only results from the SeMet dietary exposure part of the study are used here

3 - data from the low carbohydrate diet were not used as the authors reported that reduced weight of fish on this diet was likely due to food avoidance, not toxicity

BW = Body Weight

D = Deformities

FG = Feed:Gain ratio

L = Length

R = Reproduction

S = Survival

SA = Swimming Activity

Using the data presented in Table 3-3, SMCVs were calculated for each fish species. For species where only one toxicity study was reported, the SMCV is equal to the effect threshold from that study. The SMCVs are shown in the Table 3-4.

Table 3-4
Species mean chronic values calculated from the toxicity studies evaluated above.

Fish	Species	Water Type	SMCV (mg/kg-dw)		
			Liver	Muscle	Whole body
Bluegill	<i>Lepomis macrochirus</i>	fresh	18.8	5.8	5.6
Channel catfish	<i>Ictalurus punctatus</i>	fresh	9.6	3.0	3.0
Chinook salmon	<i>Oncorhynchus tshawytscha</i>	fresh	24.5	8.4	7.6
Chinook salmon	<i>Oncorhynchus tshawytscha</i>	brackish	45.3	19.3	17.1
Fathead minnow	<i>Pimephales promelas</i>	fresh	20.3	6.1	6.0
Rainbow trout	<i>Oncorhynchus mykiss</i>	fresh	42.7	1.9	7.6
Sacramento splittail	<i>Pogonichthys macrolepidotus</i>	fresh	24.8	12.3	10.8
White sturgeon	<i>Acipenser transmontanus</i>	fresh	10.5	10.8	10.6

Note: shaded cells are based (at least partly) on regressions, not measurements

Life History differences

To determine whether there is a trend in the sensitivity to selenium over the life span of a fish, the data gathered were segregated by life-history stage (e.g., adult, juvenile/fingerling, fry/larvae, egg). There were little data for fish larvae/eggs, and the majority of the available data are for effects on juveniles and adults. From the available data (Figures 3-3, 3-4) there does not appear to be a relationship between age and selenium sensitivity. A relationship may be present, but there is insufficient data available to adequately evaluate the existence of a pattern.

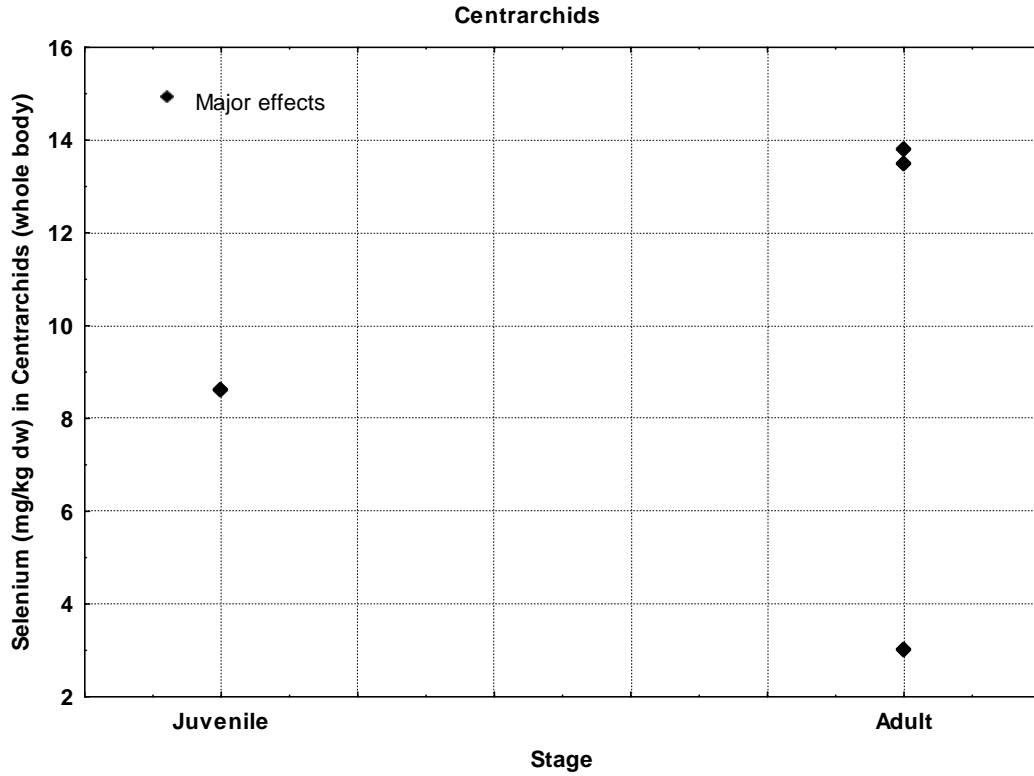


Figure 3-3 Effect thresholds for centrarchids (i.e., bluegill, green sunfish, and redear sunfish) from the selected studies grouped by life history stage.

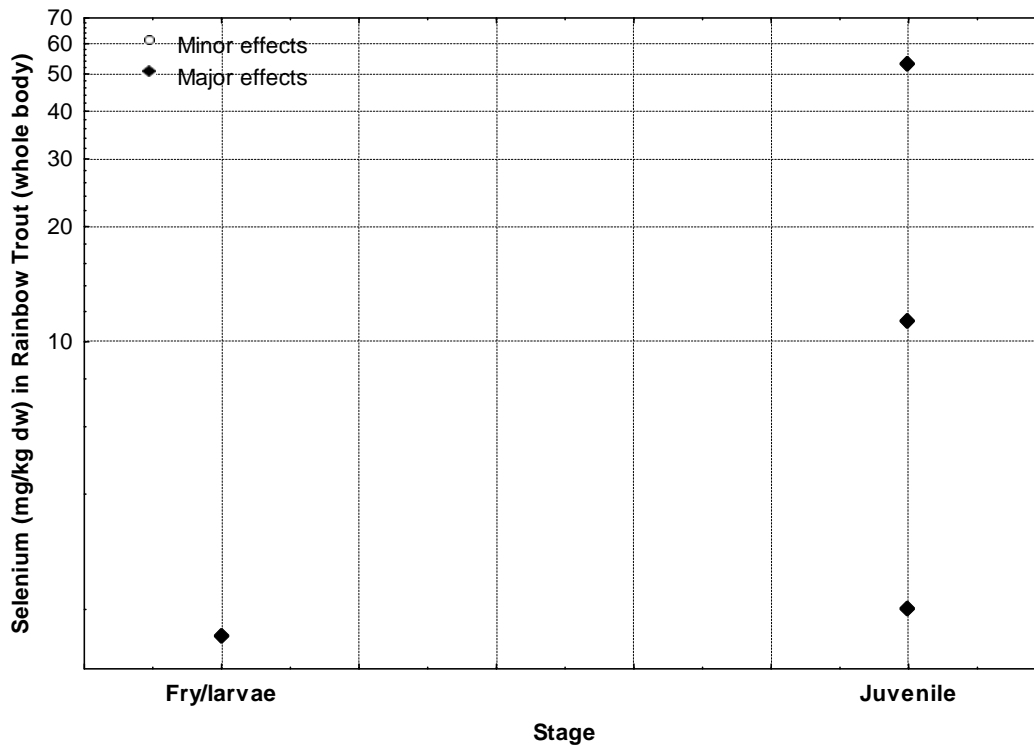


Figure 3-4 Effect thresholds for rainbow trout from the selected studies grouped by life history stage.

Since there were too few suitable studies to evaluate the potential effect of life history stage on selenium toxicity to fish, some of the criteria that had been used to exclude studies were relaxed. Specifically, criteria F and G of Table 3-1 were relaxed to increase our ability to evaluate life history stage. However, this means that studies that were included where fishes were either fed food that was not reared under controlled conditions or where fishes were exposed to selenium in water only. The results are shown in Figures 3-5 and 3-6. Note that the studies that were added by relaxing the selection criteria were not included in the calculation of SMCVs or screening values.

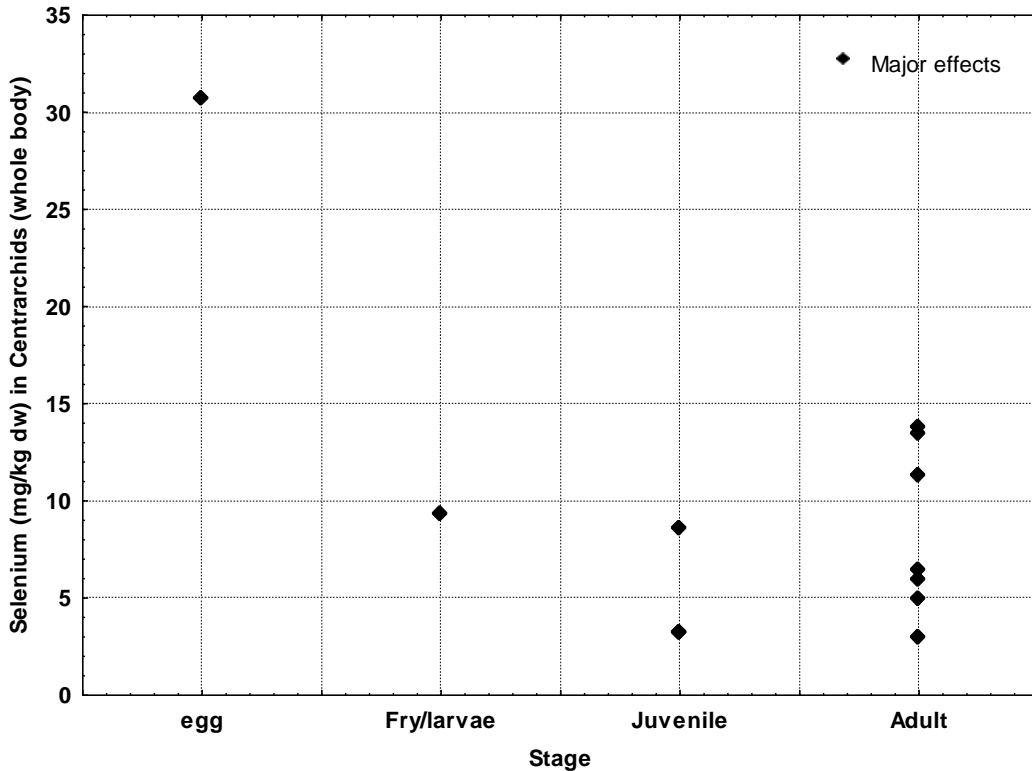


Figure 3-5 Effect thresholds for centrarchids after relaxing the selection criteria.

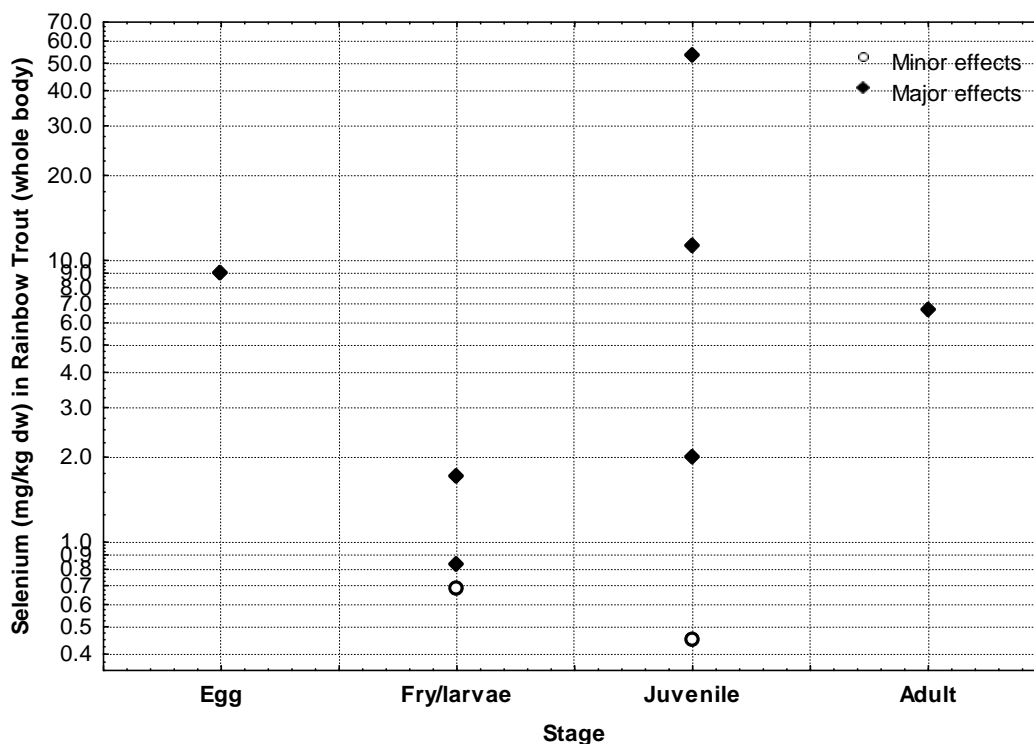


Figure 3-6 Effect thresholds for rainbow trout after relaxing the selection criteria.

Although the range of effect thresholds in Figure 3-5 overlap, the mean effect threshold for juvenile centrarchids is 1.7 times lower than for adults. No trend was apparent in the data available for rainbow trout. Overall, it does not appear that eggs are more sensitive than juvenile or larval fish. There are several potential reasons that the available data do not show that eggs are more sensitive than juvenile/larval fish: 1) the endpoints measured were not sensitive enough, 2) the type of selenium exposure was not conducive to observing effects on eggs (e.g., waterborne exposures), or 3) fish eggs may indeed be less sensitive to toxic chemicals than other life history stages (Finn 2007).

3.3 DISCUSSION

80 selenium toxicity studies were reviewed in an effort to derive selenium screening values for species representative of fishes in the North Bay (Table 3-1). Based on this review, species which are appropriate for use in developing a fish tissue screening values for the North Bay, and for which usable selenium toxicity data are available, include: bluegill (*Lepomis macrochirus*), fathead minnow (*Pimephales promelas*), rainbow trout (*Oncorhynchus mykiss*), Chinook salmon (*Oncorhynchus tshawytscha*), Sacramento splittail (*Pogonichthys macrolepidotus*), and white sturgeon (*Acipenser transmontanus*).

With the exception of the study on the impacts of selenium on Chinook salmon in fresh and brackish water (Hamilton et al. 1990), all usable studies performed to date on the effects of selenium on fish have been performed in freshwater. In addition to these species, selenium toxicity data was sought for striped bass, flounder, and delta smelt. However, no usable selenium toxicity data were available for these fish, nor were data available for any other closely related species (e.g., pond smelt, *Hypomesus olidus*).

Based on the available data, it appears that the species of concern in the North Bay for which toxicity data are available (i.e., Sacramento splittail and white sturgeon) are less sensitive to selenium than bluegill (Table 3-4), a species that has been observed to be particularly sensitive to selenium in a number of studies (e.g., Lemly 1993a) and was selected by USEPA as the basis of the current draft water quality criterion for selenium (USEPA 2004). Further, channel catfish appear to be even more sensitive to selenium than bluegill. However, with only one dietary and one injection toxicity study available on catfish, confidence in the sensitivity of channel catfish to selenium is limited.

Other selenium screening values

The selection of an appropriate selenium fish tissue screening value, protective of toxic effects in both individual fish and populations, is an area of active debate (Chapman 2007; Hamilton 2003, 2004; Lemly and Skorupa 2007; McDonald and Chapman 2007; Skorupa et al. 2004; USEPA 2004). Numerous screening values for selenium in fish tissues have been proposed in the past. These values are summarized in Table 3-5.

Table 3-5
Whole body fish tissue screening levels (mg/kg-dw) published in the scientific literature.

Reference	No effect ^a	Level of concern ^b	Toxicity Threshold ^c
Lemly and Smith (1987)			12
Henderson et al (1995)	4	4-12	12
Stephens et al. (1997)	2-3	4	4
USDOI (1998)	2-3	2-4	4
DeForest et al (1999)			6 (cold water)
DeForest et al (1999)			9 (warm water)
Lemly (1993c, 1996, 2002b)			4
Hamilton (2003)			4
Ohlendorf (2003)			4
USEPA (2004)			7.9

Notes:

- a - Concentrations less than this value produce no discernible adverse effects on fish or wildlife and are typical of background concentrations in uncontaminated environments (USDOI 1998).
- b - Concentrations in this range rarely result in discernible adverse effects on some fish or wildlife species (USDOI 1998).
- c - Concentrations greater than this value may result in adverse effects on some fish or wildlife species (USDOI 1998).

The earliest screening values were 12 mg/kg-dw (see Lemly and Smith (1987), Henderson et al. (1995)) (Table 3-5). However, as more data became available, most authors generally recommended a screening value of 4 mg/kg-dw (Table 3-5). In part, those screening values were derived to be protective of the lowest concentration at which selenium exposures resulted in toxicity in a single study. Thus, the approach used to derive the screening values in the scientific literature has generally been to use the lowest whole body values from Table 3-3. Further, the approach in the scientific literature has been to derive a screening value protective of all fish species across the entire United States and not just the North Bay.

There have also been several critiques of the USEPA (2004) draft that have noted statistical and interpretational errors in the draft that potentially affect the draft screening value (Lemly and Skorupa 2007, Skorupa et al. 2004).

Presser and Luoma (2006) also reviewed the toxicity literature and concluded that whole-body fish tissue concern levels range from 1.5 to 6 mg/kg-dw.

Warm water vs. cold water screening values

One of the major topics of discussion in the recent past has been whether cold water fish are more sensitive to selenium than warm water fish. Recent reviews have not found support for the cold vs. warm water distinction (e.g., Hamilton 2003, Chapman 2007).

Effect of sulfate on selenium toxicity

Acute toxicity tests have shown that sulfate reduces the potential for bioaccumulation and toxicity of selenium to algae, aquatic invertebrates, and fish (see Brix et al. 2001, Schlenk et al. 2003, USEPA 2004). USEPA (2004) provides the following discussion on the effects of sulfate on selenium toxicity:

“The toxicity of a number of metals (e.g., copper and cadmium) to aquatic organisms is related to the concentration of hardness in the water. The toxicity of these metals to many different aquatic species has been shown to decrease as the hardness concentration increases. A similar relationship also has been recognized between selenate and dissolved sulfate in freshwater (a similar relationship is not evident between selenite and sulfate or between either form of selenium and hardness). The studies reviewed in this document indicate that, as the concentration of sulfate increases, the acute toxicity of selenate is reduced (less toxic). Selenate acute toxicity tests conducted at different levels of dissolved sulfate are available with C. dubia, D. magna, H. azteca, G. pseudolimnaeus, chinook salmon and fathead minnows (Table 1a [of USEPA 2004]). These data indicate that, in general, selenate is more toxic to these species in low sulfate water than in higher sulfate water.”

Since sulfate levels should be higher in brackish and marine waters than in freshwaters, screening values based on freshwater selenium toxicity studies are likely to be protective of potential impacts to fishes in estuarine and marine environments. There are several possible reasons why sulfate may reduce the toxicity of selenate, including 1) the ability of sulfate, calcium, or magnesium to prevent the interaction of selenomethionine with critical subcellular proteins by maintaining the cellular redox potential (Schlenk et al. 2003) and 2) direct competition at the cell uptake site as selenate and sulfate are structurally similar group VI oxyanions of the form XO_4^- ; experiments with bacteria indicate that selenate and sulfate have a common membrane carrier and that active transport by this carrier is the only means by which selenate may enter a cell (Brix et al. 2001).

Potential screening values for the North Bay

The objective of this review of the selenium toxicity information available for fishes is to provide a technical basis for the selection of an appropriate selenium fish tissue screening value for in the North Bay. Since there are limited selenium toxicity data available for fish of concern for the North Bay (e.g., no suitable selenium toxicity data for delta smelt, halibut, jacksmelt, striped bass, Tidewater goby, or white croaker), it is not possible to develop screening values that take into account the effects of selenium on all fish species of potential concern in the North Bay.

The SMCVs for species such as Chinook salmon, rainbow trout, Sacramento splittail, and white sturgeon indicate that these species are less sensitive to selenium than bluegill and channel catfish (Table 3-4), which appear to be fairly sensitive to selenium. Thus, using a screening value for the North Bay based on either bluegill (e.g., SMCV of 5.6 mg/kg-dw whole body) or channel catfish (e.g., SMCV of 3.0 mg/kg-dw whole body) should be protective of most (if not all) fish species, while not setting an unrealistically low threshold for potential effects.

The single study that evaluated the effects of selenium in both brackish and freshwater (Hamilton et al. 1990), indicated that Chinook salmon were more than twice as sensitive to selenium in freshwater as in brackish water. However, this study examined the effects of selenium on larvae in freshwater and juveniles in brackish water. Therefore, the greater sensitivity observed in freshwater with larvae could also be due to life history differences in selenium sensitivity.

Table 3-4 also presents SMCVs for selenium in liver and muscle. Liver concentrations respond rapidly to changes in the environment and may be useful in detecting short term selenium fluctuations. Muscle concentrations may be non-destructively measured in relatively large fishes by collecting and analyzing muscle plugs. This may be desirable as it reduces the impact of selenium monitoring on fish populations, which is especially important for special status species. However, it should be noted that the regressions used here to convert selenium concentrations measured in one tissue type to another tissue type are not specific to the species and populations considered here, with the exception of white sturgeon (see Appendix A). Therefore, using screening values that were calculated using the regressions from USEPA (2004) incorporates some uncertainty.

Beckon (2007)

In contrast to the approach used here (i.e., calculating effect thresholds and SMCVs), Beckon (2007) derived an EC10 and an EC20 (of 1.84 and 2.5 mg/kg-dw, respectively) for the survival of salmon fry by performing a regression on the treatment means in Hamilton (et al. 1990) (see above). However, it should be noted that performing a regression on the treatment means artificially reduces the variation. Further, the shape of the relationship may change when using the raw data. Thus, the EC10 and EC20 derived by Beckon (2007) should be viewed as approximations. It is also unknown whether the EC10 and EC20 are significantly different from each other.

Nutritional requirements

Selenium is a micro-nutrient (see Section 1). When animals do not have enough selenium in their diet, selenium deficiency results (NRC 1993, 1994). For fish, nutrient requirements are given in terms of the concentration in their feed, not in fish tissue, as is being used here to derive screening values. Nonetheless, the nutritional requirements of two species of fish have been established and are provided here for reference: 0.25 mg/kg for channel catfish and 0.3 mg/kg for rainbow trout (NRC 1993). These concentrations are given in an "as fed basis." Fish feed is usually in the form of dry pellets and probably has a moisture content of approximately 10%, meaning the dietary requirements listed above in mg/kg-as fed do not differ substantially from mg/kg-dw.

Additional considerations

Issues to be considered in the collection and interpretation of samples include:

- tissue concentrations in fishes may vary with the time of year sampled
- tissue concentrations may vary by geographic location
- if sampling dietary items of birds, selenium concentrations may also differ among their prey items
- number of samples to collect
- the frequency of collections
- whether samples should be composited
- how to compare measured concentrations to screening values

These issues are discussed in greater detail in Section 6.

The studies used in the determination of the screening value presented above, and all screening values obtained from the literature, were not derived using the populations of fish that occur in the North Bay nor using the environmental conditions in the North Bay. This means that there is some uncertainty as to whether any screening criteria are actually applicable. Similarly, McDonald and Chapman (2007), recommend that screening values only be used to determine if further evaluation is necessary. They recommend that if fish tissue concentrations exceed an appropriate screening value that 1) reproductive toxicity testing be conducted for the species of concern and that if reproductive toxicity testing indicates that the species has been negatively affected by selenium that 2) fish population surveys be conducted. McDonald and Chapman (2007) provide recommendations on how both reproductive toxicity testing and fish population surveys can be integrated into a selenium monitoring program.

Future research and data gaps

Several data gaps and areas where further research may be beneficial to the Water Board were identified during the evaluation of selenium toxicity to fish in the North Bay, as follows:

1. Although it is believed that selenium should be less toxic to fish in marine and estuarine systems than freshwater systems, the data to show this are lacking. Toxicity experiments performed with representative fish species in using multiple salinities over the range that occurs in the North Bay would provide valuable information.
2. Toxicity studies have not been performed on most of the species of concern (which includes endangered species) in the North Bay. Thus, this report has assumed that toxicity studies on bluegill, rainbow trout, chinook salmon, channel catfish, and

fathead minnows are representative of the species of concern. The species of concern may be more or less sensitive.

3. Channel catfish appear to be one of the most sensitive species. However, only two studies were available. If the Water Board believes that channel catfish are representative of the fish in the North Bay, additional toxicity studies using channel catfish would be warranted.
4. The existing toxicity data suggests that at younger life history stages are more sensitive to selenium, but most selenium toxicity studies have focused on only a single life history stage. Thus, it is possible that some species may be more sensitive to selenium than shown here.
5. Species-specific regressions to convert selenium concentrations from one tissue type to another are lacking for all of the fish species evaluated here, except white sturgeon. Therefore, the regressions from USEPA (2004) for bluegill were used for most species. Since the applicability of these regressions to other species is unknown, screening values derived using the bluegill tissue relationships should be viewed as approximations and may need to be revisited as new data becomes available. Further, if the Water Board decides to monitor fish tissue concentrations by collecting muscle plugs, it would be beneficial to develop species-specific regressions.
6. A detailed re-analysis of the published toxicity data using, for example, biphasic regressions (Beckon 2007, Beckon et al. 2008) would provide a greater level of confidence in estimates of the threshold for toxic effects of selenium vs. a LOAEL, NOAEL, or effect threshold. However, if only the treatment means are available for the analyses, it should be remembered that this type of analysis will mask the true variability in the data.

3.4 CONCLUSIONS

Exposure to elevated levels of selenium can cause adverse effects in fish. Two of the species that occur in the North Bay that have been tested (i. e., Sacramento splittail and white sturgeon) appear to be less sensitive than other freshwater fish. While it has generally been believed that bluegill are one of the more sensitive fish species, the two studies available on channel catfish indicates that they may be more sensitive than bluegill. However, one of the most important concerns for selenium toxicity to fish remains an open question at the end of this review: is selenium less toxic to fish in marine and brackish waters than freshwater? The available data supports the assertion that selenium should be less toxic to fish in marine and brackish waters, but it is not possible to quantify the difference at this point.

Numerous selenium screening values protective of fish have been proposed. For whole body fish selenium concentrations, the recommended screening values are usually in the range of 2-4 mg/kg-dw (Table 3-5). Additionally, it has been proposed that separate screening values be used for cold water fish vs. warm water fish, although recent reviews have not found support this distinction (e.g., Hamilton 2003, Chapman 2007).

Based upon the data presented here, there are several options for selenium fish tissue screening values. Those options are as follows (all in units of mg/kg-dw whole body):

1. The lowest SMCV: 3.0 (Table 3-4)
2. The salmon EC20 from Beckon (2007) of 2.5
3. Lowest concentration at which adverse effects were reported (Table 3-3)
 - a. LOAEL of 2.3
4. The lowest LOAELs for fish in the North Bay (Table 3-3)
 - a. 12.9 for Sacramento splittail
 - b. 12.3 for white sturgeon
5. The lowest effect thresholds for fish in the North Bay (Tables 3-3, 3-4)
 - a. 10.8 for Sacramento splittail
 - b. 6.2 for white sturgeon
6. The lowest SMCVs for fish in the North Bay (Table 3-4)
 - a. 10.8 for Sacramento splittail
 - b. 10.6 for white sturgeon
7. The white sturgeon EC10 calculated by Beckon (2008) from the data in Linville (2006) of 11.9

The choice of using an SMCV, LOAEL, or effect threshold is dependent upon both the level of risk and uncertainty the Water Board wishes to accept. This issue was discussed in more detail in the Introduction. It is worth noting that of these values, only the LOAELs represent concentration at which effects have been demonstrated. However, since only a few concentrations have been tested, effects may actually occur at lower concentrations.

4 AVIAN TOXICITY REVIEW

The waters of the North Bay supports a diverse avian biota. Some birds are residents in the Bay all year round, while many others rely on the North Bay as part of their annual migrations. The birds supported include both game birds as well as threatened and endangered species. The North Bay supports the following threatened and endangered bird species (USFWS 2007):

- American bittern (*Botaurus lentiginosus*)
- American peregrine falcon (*Falco peregrinus anatum*)
- American white pelican (*Pelecanus erythrorhynchos*)
- bald eagle (*Haliaeetus leucocephalus*)
- black tern (*Chlidonias niger*)
- California black rail (*Laterallus jamaicensis coturniculus*)
- California brown pelican (*Pelecanus occidentalis californicus*)
- California clapper rail (*Rallus longirostris obsoletus*)
- California least tern (*Sterna antillarum browni*)
- double-crested cormorant (*Phalacrocorax auritus*)
- marbled murrelet (*Brachyramphus marmoratus*)
- mountain plover (*Charadrius montanus*)
- northern harrier (*Circus cyaneus*)
- osprey (*Pandion haliaetus*)
- prairie falcon (*Falco mexicanus*)
- tricolored blackbird (*Agelaius tricolor*)
- western least bittern (*Ixobrychus exilis hesperis*)
- western snowy plover (*Charadrius alexandrinus*)
- white-faced ibis (*Plegadis chihi*)
- white-tailed kite (*Elanus leucurus*)

The North Bay supports a number of birds that are not classified as threatened and endangered but are covered under the Migratory Bird Treaty Act (MBTA), including (USFWS 2007):

- Aleutian Canada goose (*Branta canadensis leucopareia*)
- black scoter (*Melanitta nigra*)
- Caspian tern (*Sterna caspia*)
- greater scaup (*Aythya marila*)
- lesser scaup (*Aythya affinis*)
- surf scoter (*Melanitta perspicillata*)
- white-winged scoter (*Melanitta fusca*)

Lastly, the North Bay supports several species of water fowl that are of recreational interest. While the California Department of Fish and Game (DFG) does not provide any information on which species are harvested in the North Bay, they do provide limits (i.e., “bag limits”) on how many can be harvested at one time (DFG (2007)). These limits, which indicate which water fowl species are of recreational interest, are provided below:

- canvasback (*Aythya valisineria*): 1
- American coot (*Fulica americana*): 25
- Ross’s goose (*Chen rossii*): 4
- snow goose (*Chen caerulescens*): 4
- white-fronted goose (*Anser albifrons*): 4
- cackling goose (*Branta hutchinsii*): 6
- Aleutian goose (*Branta canadensis leucopareia*): 6
- Canada goose (*Branta canadensis*): 4
- mallard (*Anas platyrhynchos*): 7 but not more than 2 hens
- common moorhen (*Gallinula chloropus*): 25
- pintail (*Anas acuta*): 1
- redhead (*Aythya americana*): 2

- scaup (*Athya affinis* and *Athya marila*): 3
- merganser (*Mergus spp.* and *Lophodytes cucullatus*): 7

The USFWS (2007) evaluated the bird species found in the North Bay that are covered under the MBTA as well as the threatened and endangered species and determined that the following species were most at risk from potential exposures to selenium:

- bald eagle (*Haliaeetus leucocephalus*)
- black scoter (*Melanitta nigra*)
- California clapper rail (*Rallus longirostris obsoletus*)
- greater scaup (*Aythya marila*)
- lesser scaup (*Aythya affinis*)
- surf scoter (*Melanitta perspicillata*)
- white-winged scoter (*Melanitta fusca*)

Among birds, exposures to elevated levels of selenium can induce gross abnormalities during development, egg inviability, chick mortality (Adams et al. 2003), reduced weight gain, reduced adult condition, and reduced adult survival (NRC 2005, Ohlendorf 2003). When the selenium concentrations are high enough in a large enough area, these effects can lead to population declines for the most affected species.

The step in the effort to determine whether birds may be adversely impacted by selenium in the North Bay is to evaluate the toxicity of selenium to the marine mammals. Next, potential selenium screening values for the species in the North Bay are proposed. Lastly, the screening values are compared to nutritional requirements.

4.1 METHODS

Selenium toxicity data for the bird species that the USFWS (2007) has identified as being most at risk from selenium in the North Bay (see list above) would be the most relevant for the Water Board's development of a TMDL. However, selenium toxicity studies have not been performed for any of the species identified by the USFWS (2007) as being most at risk from selenium in the North Bay. Therefore, in this section of the report, we review the available avian selenium toxicity literature.

For birds, selenium studies have generally focused on 1) determining a toxic concentration in the diet, 2) determining a toxic concentration in eggs, or 3) improving bird "performance" on a poultry farm. We reviewed papers published in the scientific literature for all three types of data. Studies were excluded from the consideration for the selection of a screening value (see Table 4-1) if they:

- A. did not provide a LOAEL

- B. were not chronic
- C. exposed birds to multiple contaminants simultaneously
- D. exposed birds to multiple treatments simultaneously
- E. field studies

Using the filtering criteria above, only studies where the reported effects can unambiguously be attributed to selenium were reviewed. Some of the poultry performance studies were not performed using dietary concentrations high enough to cause toxic effects. These studies will be used to set a lower bound on screening values. Most of the studies describing the early laboratory work on the effects of selenium on poultry species are no longer readily accessible. When the original studies are not readily available, the reviews that summarize the results of the original studies are cited.

The reported effects from each study were grouped into one of two categories: major and minor effects. Major effects are those that have the potential to impact birds at the organism and/or population level (e.g., increased mortality, reduced fecundity, reduced growth, etc.). Minor effects are those that are measurable, but are unlikely to result in population level effects and/or the long-term impacts on individual bird performance was unclear (e.g., a change in an enzyme concentration). Where both major and minor effects were observed at the same concentration, the effects were assumed to be major. Only major effects were considered in development of screening values.

All studies that were reviewed are listed in Table 4-1. Studies that were determined to be unsuitable are noted in Table 4-1 using the designations from the list above. The 21 suitable studies selected are presented in Table 4-2.

Table 4-1
Selenium toxicity studies evaluated in this review. Studies that were excluded from review are indicated in the table (see text above for an explanation of the criteria).

Study	Reference	Evaluation criteria failed	Study	Reference	Evaluation criteria failed
1	Albers et al. (1996)		24	Latshaw et al. (2004)	
2	Anteau et al. (2007)	A,C,E	25	Lowry and Baker (1989)	
3	Biswas et al. (2006)	A	26	Ort and Latshaw (1978)	
4	Elzubier and Davis (1988)		27	O'Toole and Raisbeck (1997)	
5	Fairbrother et al. (1994)	C,E	28	Pappas et al. (2005)	A
6	Franson et al. (2007)		29	Paton et al. (2002)	A
7	Green and Albers (1997)		30	Payne et al. (2005)	A
8	Harding (2007)	E	31	Ratti et al. (2006)	A,E
9	Heinz and Hoffman (1996)		32	Rattner et al (2000)	A,C,E
10	Heinz and Hoffman (1998)		33	Ryu et al. (2005)	A
11	Heinz et al. (1987)		34	Sahin and Kucuk (2001)	A
12	Heinz et al. (1988)		35	Santolo et al. (1999)	A
13	Heinz et al. (1989)		36	Stanley et al. (1994)	
14	Heinz et al. (1996)		37	Stanley et al. (1996)	
15	Hoffman and Heinz (1998)		38	Stoewsand et al. (1978a)	A,C
16	Hoffman et al. (1991)		39	Stoewsand et al. (1978b)	A,C
17	Hoffman et al. (1992a)		40	Surai et al. (2006)	A
18	Hoffman et al. (1992b)		41	Takekawa et al. (2002)	A,C,E
19	Hoffman et al. (1996)		42	Wayland et al. (2002)	A,C,E
20	Hoffman et al. (1998)	C,E	43	Wiemeyer and Hoffman (1996)	
21	Hoffman et al. (2002)	C,E	44	Wilson et al. (2007)	A,C,D,E
22	Jensen (1975)		45	Yamamoto and Santolo (2000)	A
23	Kinder et al. (1995)	D	46	Yamamoto et al. (1998)	A

To be consistent with the approach used for developing screening values for fish, effect thresholds were calculated as the geometric mean of the NOAEL and LOAEL reported for the same effect in an individual study. Additionally, species mean chronic values (SMCVs) were calculated as the geometric mean of the effect thresholds (USEPA 1985). Studies in which a zero concentration was reported in the control were assumed to have used 0.2 mg/kg-dw, as this is the dietary requirement for birds (NRC 1984). Studies that did not report a NOAEL were excluded from the calculation of an effect threshold and the SMCV. Note that excluding studies in which a NOAEL was not reported from the calculation of the SMCV results in lower SMCVs.

Conversions from dry weight to wet weight are detailed in Appendix A.

4.2 RESULTS

Toxicity studies

The toxicity studies from Table 4-1 that were included in the evaluations below included the following bird species:

- Chickens
- Eiders
- Kestrels
- Pheasants

- Mallards
- Screech owls

In contrast to the studies on fish, where whole body selenium concentrations are usually measured, the toxicity studies performed on birds have usually measured the selenium content of the feed given to the bird. Therefore, the screening values derived here are for dietary selenium concentrations.

Chickens

Four studies were identified for domestic chickens (Table 4-2). Only one study (Ort and Latshaw 1978) examined the effect of selenium on the most sensitive endpoint; i.e., egg hatchability. It is also worth noting that Ort and Latshaw (1978) review two earlier studies not available to us that show 1) “egg weight, fertility and hatchability were all significantly decreased by 8 ppm [dietary] selenium,” and 2) “Embryonic development was adversely affected by 10 ppm dietary selenium but not by 5 ppm .”

Table 4-2
Summary of dietary selenium toxicity studies evaluated in this review.

Bird	Study	Life stage	Dietary form	(mg/kg-dw)			Effect		Endpoint
				NOAEL	LOAEL	Effect threshold	Major	Minor	
Chicken	4	Chick	selenite	0.15	10	1.2	X		BW
Chicken	22	Chick	selenite	0.9	4.3	2.0	X		BW
Chicken	22	Chick	selenite	4.3	13.5	7.6	X		BW, S
Chicken	25	Chick	selenite; SeMet	0.2	15	1.7	X		BW
Chicken	26	Adult	selenite	3	5	3.9	X		R
Common eider	6	Adult	SeMet	20.6	57.7	34.5	X		BW
Mallard	1	Adult	SeMet	22.3	44.7	31.6	X		C
Mallard	7	Adult	SeMet	11.2	22.3	15.8	X		S
Mallard	9	Adult	SeMet	0.6	10.6	2.6	X		R
Mallard	10	Adult	SeMet	0.4	9.8	2.1	X		R
Mallard	11	Adult	selenite	10.9	27.3	17.3	X		BW, R
Mallard	11	Adult	SeMet	0.2	10.9	1.5	X		R
Mallard	12	Duckling	selenite	10.9	21.6	15.3	X		BW
Mallard	12	Duckling	SeMet	10.9	21.6	15.3	X		BW
Mallard	13	Adult	SeMet	4.6	9.0	6.4	X		R
Mallard	14	Duckling	SeMet	17.0	33.7	24.0	X		BW
Mallard	15	Adult	SeMet	0.4	11.6	2.3		X	E
Mallard	16	Duckling	SeMet; low protein	0.2	16.9	1.9	X		BW
Mallard	16	Duckling	SeMet	16.9	66.9	33.6	X		BW, S
Mallard	17	Duckling	SeMet	0.2	16.9	1.9	X		BW
Mallard	18	Duckling	SeMet	0.2	16.5	1.9		X	E
Mallard	18	Duckling	SeMet	16.5	65.4	32.9	X		BW
Mallard	18	Duckling	SeMet; low protein	16.5	65.4	32.9	X		S
Mallard	18	Duckling	SeMet; low protein	0.2	16.5	1.9		X	E
Mallard	18	Duckling	SeMet; high protein	0.2	16.5	1.9	X		BW
Mallard	19	Duckling	SeMet, Se yeast, Se in wheat	0.2	16.9	1.9		X	E
Mallard	27	Flightling	SeMet	13.8	33.8	21.6	X		BW, S
Mallard	36	Adult	SeMet	0.37	6.5	1.6	X		R
Mallard	37	Adult	SeMet	3.9	7.8	5.5	X		BW, R
Pheasant ¹	24	Adult	unknown	0.4	9.3	1.9	X		R, S
Screech owl	43	adult	SeMet	8.8	30	16.2	X		BW, R
Screech owl	43	adult	SeMet	0.3	8.8	1.6		X	E

Notes: 1 - Although the concentration at the NOAEL was not measured, the lead investigator on this study said that he believes it was probably 0.4 mg/kg.

BW = Body Weight

C = Condition

D = Deformities

E = Enzymes

FG = Feed:Gain ratio

L = Length

R = Reproduction

S = Survival

SA = Swimming Activity

In addition to the studies summarized in Table 4-2, the NRC (1980, 1994, 2005) provide summaries of additional dietary selenium toxicity studies on domestic chickens that were not available to the authors of this report. These data are presented in Tables 4-3 through 4-5, respectively.

Table 4-3
Summary of additional selenium toxicity studies from the NRC (1980).

Age	Chemical Form	Concentration (mg/kg)		Effect	Reference
		NOAEL	LOAEL		
Adult	Se in corn, barely, wheat	2.5	5	increased chick mortality	Moxon (1937)
Adult	Na ₂ SeO ₃	-	6.5	deformed embryos	Moxon (1937)
1 day	Na ₂ SeO ₃	4	8	decreased weight gain	Moxon (1937)
1 day	selenous acid	2	8	increased chick mortality	Thapar et al (1969)
1 day	SeO ₂	-	5	increased mortality	Hill (1979)
Adult	Na ₂ SeO ₃	-	8	embryo necrosis	Gruenwald (1958)

Table 4-4
Summary of additional selenium toxicity studies from the NRC (1994).

Age	Chemical Form	Concentration (mg/kg)	Effect	Reference
Immature	Na ₂ SeO ₃ + Se in wheat	10	Reduced growth	Carlson and Leitis (1957)
Laying hen	Se in wheat	10	Reduced hatchability	Moxon and Wilson (1944)

Table 4-5
Summary of additional selenium toxicity studies from the NRC (2005).

Age	Chemical Form	Concentration (mg/kg)		Effect	Reference
		NOAEL	LOAEL		
Adult	selenite	5	10	reduced growth	Jensen and Chang (1976)
1 day	selenite	1	5	reduced growth	Jensen (1986)

For all of the studies on chickens presented above, it is unclear whether the dietary concentrations are provided as ww or dw. It is likely that the dietary concentrations are ww but that the %moisture is relatively low (e.g., 10%) as chicken feed is usually in the form of dry pellets. So, there is some uncertainty about the exact concentration of selenium in the studies above on chickens, but it is likely to be a small effect; e.g., 5 mg/kg-ww with a %moisture of 10% is equivalent to 5.6 mg/kg-dw.

Eiders

A single suitable study was identified (Franson et al. 2007). That study provided both a NOAEL and LOAEL for weight loss (i.e., a major effect) in diet, but did not examine reproductive success (Table 4-2).

Kestrels

Three studies have been conducted on the toxicity of dietary selenium to kestrels (Santolo et al. 1999, Yamamoto et al. 1998, Yamamoto and Santolo 2000). The first two studies (i.e., Santolo et al. 1999, Yamamoto et al. 1998) did not show an effect at up to 12 mg/kg-dw. In the third study (Yamamoto and Santolo 2000), the authors state that kestrels fed 12 mg/kg-dw selenium had a lower “normalized body fat” than the kestrels in the other treatments.

However, the difference was not significant (i.e., $p = 0.173$) and was, therefore, excluded from Table 4-2 and consideration in the development of a screening value.

Mallards

Mallards are the bird species for which the most information is available. Fourteen suitable studies were identified on mallards. The studies examined effects on adults, ducklings, and reproductive success (Table 4-2).

Pheasants

A single suitable study was identified (Latshaw et al. 2004). That study provided a NOAEL and LOAEL based on mortality and reduced egg laying (Table 4-2).

Screech owls

A single suitable study was identified (Wiemeyer and Hoffman 1996). That study provided both a NOAEL and LOAEL for selenium in the diet and eggs based on weight loss and reduced reproductive success. A NOAEL and LOAEL was also provided for minor effects; i.e., changes in enzyme concentrations (Table 4-2).

4.3 IMPROVED PERFORMANCE STUDIES

Among birds that are raised on poultry farms, there has been extensive research in an attempt to balance the beneficial effects of selenium supplementation against the toxicity of selenium. These studies generally provide NOAELs only and do not necessarily examine the effects of selenium on reproductive success. The available studies are summarized in Table 4-6 below.

Table 4-6
Studies evaluating improved performance in poultry from selenium supplementation.

Bird	Study	Life stage	Dietary form	NOAEL (mg/kg)	dw/ww	Effects			
						Survival	Weight	Egg output	Reproductive success
Chicken	24	Adult	selenite	2.6	?			X	
Chicken	24	Adult	Se-yeast	2.9	?			X	
Chicken	27	1 day	selenite	8.17	dw		X		
Japanese quail	3	1 day	selenite	1.2	?	X	X		
Japanese quail	28	10 day	selenite	0.2	dw		X		

The most sensitive endpoint for selenium effects in birds is reproductive success (i.e., egg hatchability and chick survival). However, since none of the performance studies examined the potential effects of selenium on reproductive success, these studies should not be used to put a lower bound on the acceptable level of dietary selenium for birds.

4.4 DISCUSSION

More than 40 selenium toxicity studies were reviewed in an effort to determine dietary selenium screening values for species representative of birds in the North Bay (Table 4-1). Based on this review, species which are appropriate for use in developing screening criteria for the North Bay, and for which usable selenium toxicity data are available, include:

chickens (*Gallus gallus*), common eiders (*Somateria mollissima*), mallards (*Anas platyrhynchos*), pheasants (*Phasianus colchicus*), and screech owls (*Otus asio*).

The data presented above (Tables 4-2 through 4-5; regardless of selenium type) were grouped into effects on immature birds (i.e., chicks and ducklings), adults, and reproductive success (i.e., egg hatchability, chick survival, egg fertility, etc.) and are presented in Table 4-7 below.

Table 4-7
Summary of NOAELs and LOAELs (mg/kg-dw) reported in this section grouped by whether the effects were measured in chicks/ducklings, adult birds, or in terms of reproductive success. Studies using all selenium species are shown here.

	Chick/Duckling			Adult			Reproductive success		
	NOAEL	LOAEL	Effect Threshold	NOAEL	LOAEL	Effect Threshold	NOAEL	LOAEL	Effect Threshold
Chicken	0.15	10	1.2	5	10	7.1	2.5	5	3.5
	0.2	15	1.7				3	5	3.9
	0.9	4.3	2.0				5	10	7.1
	1	5	2.2				-	6.5	-
	2	8	4.0				-	8	-
	4	8	5.7				-	8	-
	4.3	13.5	7.6				-	10	-
	-	5	-						
	-	10	-						
			SMCV	2.9			SMCV	7.1	
Eider				20.6	57.7	34.5			
Mallard	0.2	16.5	1.9	11.2	22.3	15.8	0.2	10.9	1.5
	0.2	16.9	1.9	13.8	33.8	21.6	0.37	6.5	1.6
	0.2	16.9	1.9	22.3	44.7	31.6	0.4	9.8	2.1
	10.9	21.6	15.3				0.6	10.6	2.6
	10.9	21.6	15.3				3.9	7.8	5.5
	16.5	65.4	32.9				4.6	9.0	6.4
	16.5	65.4	32.9				10.9	27.3	17.3
	16.9	66.9	33.6						
	17.0	33.7	24.0						
			SMCV	10.4			SMCV	22.1	
Pheasant									
Screech owl							0.4	9.3	1.9
							8.8	30	16.2

From the data presented in Table 4-7, it would appear that immature chickens are more sensitive to selenium than immature mallards, although there was some variation among chicken strains (see Table 4-2). The available studies on reproductive success appear to indicate that mallards are a little more sensitive than chickens but that screech owls are less sensitive than either chickens or mallards. For pheasants, the small amount of available data indicates that reproductive success is affected at relatively low concentrations.

State of Utah

The State of Utah is also deriving dietary selenium screening values protective of birds feeding at the Great Salt Lake (Ohlendorf 2007, provided as Appendix B). To develop a selenium screening value for the Great Salt Lake, the Great Salt Lake Science Panel compiled the concentration of selenomethionine in feed, total selenium in eggs, and mean hatching success per treatment from 6 studies on mallards (i.e., Heinz et al. 1987, 1989, Heinz and Hoffman 1996, 1998, Stanley et al. 1994, 1996; all of these studies are included in Tables 4-1, 4-2, and 4-7) and examined the data using both a logistic regression and a

hockey-stick regression. The regressions were used to derive concentrations at which 10% of the population would be affected (EC10) for both dietary and egg selenium concentrations. The results for mean hatching success are as follows (mg/kg-dw):

- Dietary selenium
 - Logistic regression: 4.9
 - Hockey stick-regression: 4.4
- Egg selenium
 - Logistic regression: 12.5
 - Hockey stick-regression: 11.5

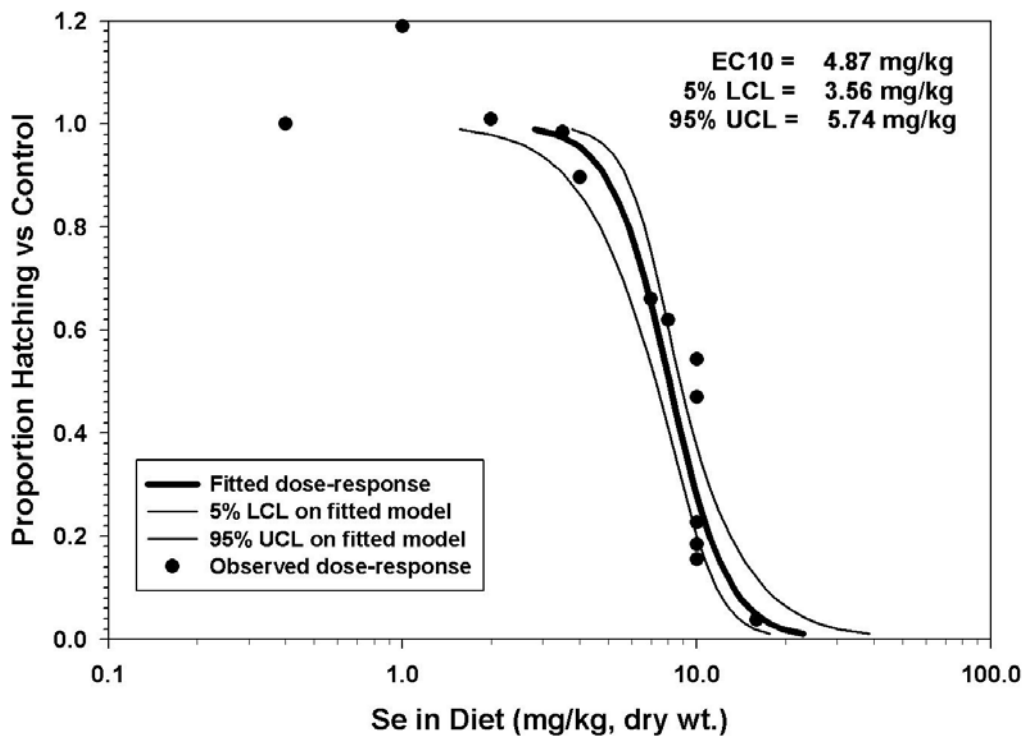


Figure 4-1 Logistic regression of mallard dietary selenium concentration vs. proportion of eggs hatching. From Ohlendorf (2007).

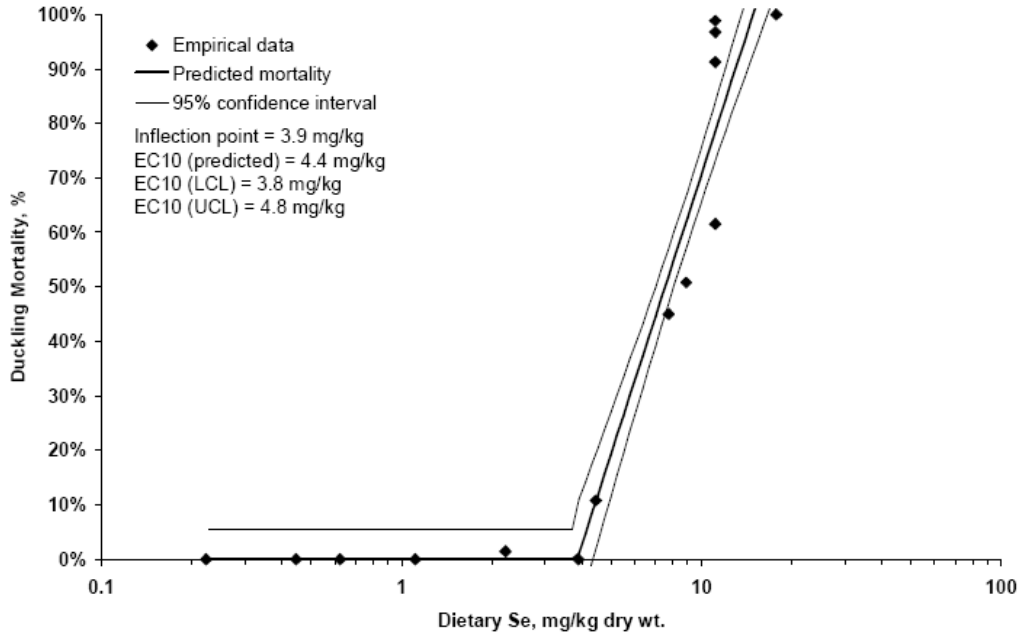


Figure 4-2 Hockey stick regression of mallard dietary selenium concentration vs. proportion of eggs hatching. From Ohlendorf (2007).

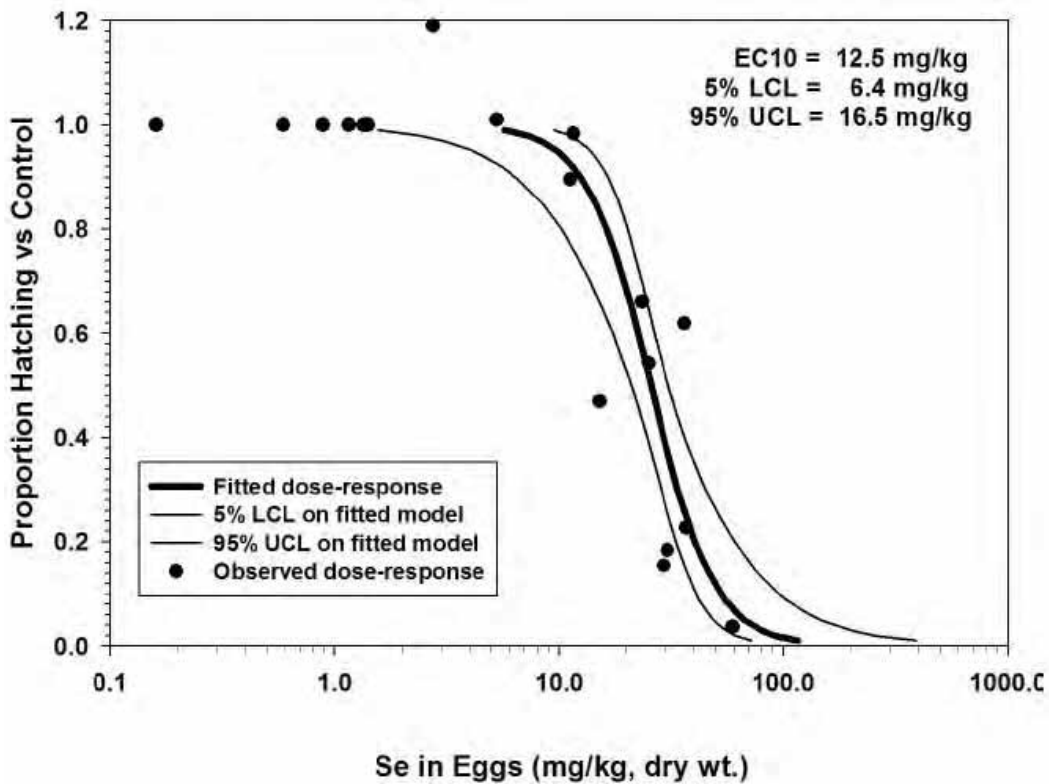


Figure 4-3 Logistic regression of mallard egg selenium concentration vs. proportion of eggs hatching. From Ohlendorf (2007).

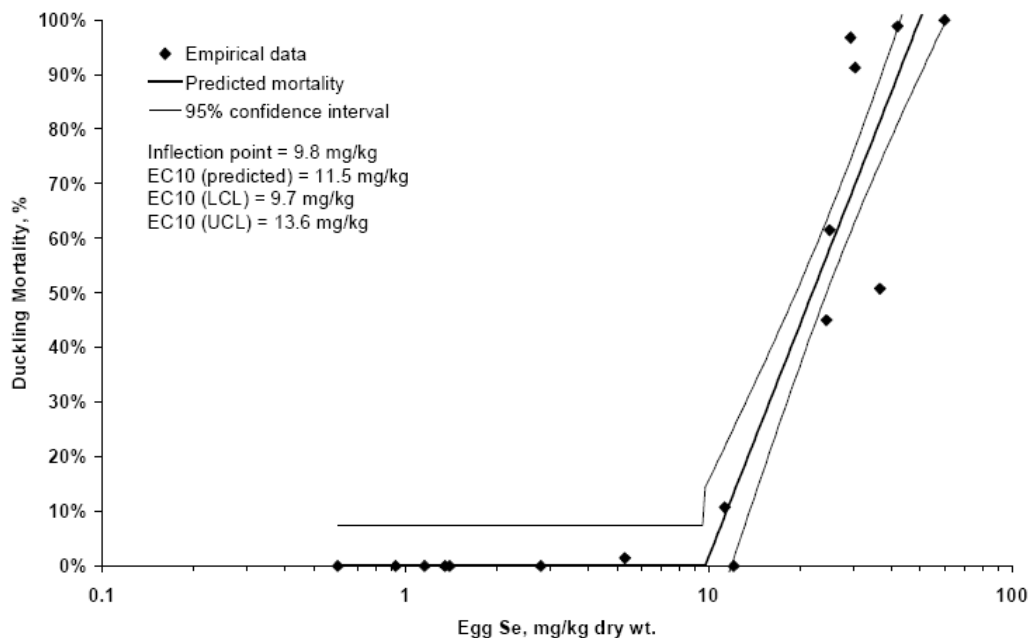


Figure 4-4 Hockey stick regression of mallard egg selenium concentration vs. proportion of eggs hatching. From Ohlendorf (2007).

The logistic regressions were previously reported in Ohlendorf (2003) and the hockey-stick regression for egg selenium was previously reported in Adams et al. (2003). The paper by Adams et al. (2003) is the third paper published by the same group of authors on this topic; i.e., Fairbrother et al. (1999, 2000) used the data from fewer studies (i.e., Heinz et al. 1989 and Stanley et al. 1994) to derive an EC10 for eggs of 16 mg/kg-dw.

As discussed above for the regression approach used by Beckon (2007) to analyze fish data, the State of Utah (Ohlendorf 2007) performed regressions on the treatment means, instead of the raw data from each individual, which artificially reduces the variation; i.e., the confidence limits on the regression lines in Figures 4-1 through 4-4 may be much larger. Further, the shape of the relationship may change when using the raw data. Thus, the EC10 and EC20 presented in Figures 4-1 through 4-4 should be viewed as approximations. Lastly, the data used in the logistic regressions (Ohlendorf 2003) was also normalized against the controls. This may have obscured a biphasic relationship (see Beckon et al. (2008)).

There are a few minor problems with the data used by the State of Utah (Ohlendorf 2007) that should be kept in mind. First, the concentration of selenomethionine used in the logistic regressions was assumed by the State of Utah (see Ohlendorf 2003) to be dry weight (Ohlendorf 2007) but the concentrations were actually presented as wet weight. The State of Utah (Ohlendorf 2007) acknowledged this by stating that the values derived in the logistic regressions for dietary concentrations should be increased by 11 percent (i.e., to 5.4 mg/kg-dw). Further, the State of Utah (see Ohlendorf 2003) used the “nominal” selenium concentrations added to feed in their analyses and not the measured concentrations. This adds an additional layer of uncertainty to the thresholds reported by the State of Utah (Ohlendorf 2007) as the actual concentration can differ from the nominal concentration either positively or negatively, depending upon the individual treatment.

Other selenium screening values

The National Irrigation Water Quality Control Program (NIWQP) recommends a lower screening value for selenium in bird eggs than the State of Utah; i.e., 6 mg/kg-dw (NIWQP 1998). The USGS (Seiler et al. 2003) used logistic regressions to derive threshold concentrations for selenium induced teratogenicity (a less sensitive endpoint than hatching success) in bird eggs collected from several selenium-impacted field sites across California (Table 4-8). The NIWQP also recommends a screening value for dietary selenium of 3 mg/kg-dw. Presser and Luoma (2006) also reviewed the toxicity literature and concluded that dietary “concern levels range from 2 to 7” mg/kg-dw for birds.

Table 4-8
Selenium screening values for teratogenesis in bird eggs (mg/kg-dw) (Seiler et al. 2003).

Bird	EC01	EC10
Ducks	15	23
Black-necked stilts	14	37
American avocets	41	74

Allometric adjustment for dietary concentrations

The species of concern in the North Bay identified by USFWS (2007) have not been examined in selenium toxicity studies. One approach for applying screening values developed for one species to another species is to allometrically adjust the screening values (Sample and Arenal 1999). This adjusts for differences in body weight, metabolism, pharmacokinetics, and sensitivity to provide the best available estimates of species-specific toxicity. The equations used to perform the allometric adjustments, and parameter values, are provided in Appendix C.

Allometric adjustments were applied to predict dietary selenium screening values for the species of concern in the North Bay identified by USFWS (2007) from three example dietary toxicity values protective of reproductive success:

1. the EC10 for mallards fed selenomethionine derived using a hockey-stick regression by Adams et al. (2003) and used by the Great Salt Lake Science Committee (Ohlendorf 2007);
2. the effect threshold (Table 4-2) derived from the study by Ort and Latshaw (1978) for chickens, and;
3. the effect threshold (Table 4-2) derived from the study by Wiedemeyer and Hoffman (1996) for screech owls.

These studies were chosen as the most representative of the available toxicity data although other toxicity values may also be used (e.g., the SMCV for chicken reproductive studies). However, since reproductive success is the most sensitive endpoint in birds, it is recommended that the allometrically adjusted dietary threshold all be based on that endpoint. The allometrically adjusted screening values are presented below in Table 4-9.

Table 4-9
Allometrically adjusted dietary selenium screening values.

Bird species	Dietary Screening Value (mg/kg-dw) Allometrically Adjusted from		
	Mallard ^a	Chicken ^b	Screech Owl ^c
Bald eagle	9.7	4.0	104.3
California clapper rail	2.2	0.9	-
Greater scaup	3.9	1.6	-
Lesser scaup	3.2	1.3	-
White-winged scoter	5.6	2.3	-
Surf scoter	4.1	1.7	-
Black scoter	3.9	1.6	-

Notes:

a - EC10 for reduced hatching success from Adams (2003) and Ohlendorf (2007) of 4.4 mg/kg-dw

b - effect threshold for reduced hatching success of 3.9 mg/kg-dw from Ort and Latshaw (1978) (Table 4-2)

c - effect threshold for reduced hatching success of 17.3 mg/kg-dw from Wiemeyer and Hoffman (1996) (Table 4-2)

Note that allometric adjustments are used to adjust dietary screening values (Sample and Arenal 1999) and are not used to adjust screening values for selenium in eggs. Further, there is some uncertainty associated with the use of allometric scaling as the allometric scaling factor used here was developed for acute toxicity data its "...applicability to chronic toxicity data is unknown. The modes of action for acute and chronic effects differ for many chemicals. As a consequence, it is likely that scaling factors based on chronic toxicity data will also differ from those based on acute toxicity data" (Sample and Arenal 1999). It should also be noted that the allometric scaling factor used here is not specific to selenium, but a mean value for other contaminants.

Allowable limits in bird feed

The FDA has approved the use of sodium selenate, sodium selenite, and selenium yeast at up to 0.3 mg/kg for chickens, swine, turkeys, sheep, cattle, and ducks (21CFR573.920). The major (i.e., 60-80%) form of selenium in selenium yeast is selenomethionine (Capelo et al. 2004, McSheehy et al. 2005, Polatajko et al. 2005).

Nutritional requirements

Selenium is a micro-nutrient. When animals do not have enough selenium in their diet, selenium deficiency results; i.e., poor growth, muscular dystrophy, and chick mortality (Ullrey 1992, NRC 1994). Due to the economic importance of the poultry industry, the nutritional requirements to maintain an adequate growth rate and normal metabolism of some of the more widely raised species have been established by the NRC (1994; see Table 4-10 below).

Table 4-10
Selenium nutritional requirements for commercially reared birds (mg/kg-dw).

Species	Strain	Age (weeks)			
		0-2	2-4	4-6	6-
Chicken	Leghorn white egg-laying	0.17	0.17	0.17	0.17
Chicken	Leghorn brown egg-laying	0.16	0.16	0.16	0.11
Chicken	Broiler	0.17	0.17	0.17	0.17
Turkey	-	0.22	0.22	0.22	0.22
Duck	-	0.22	-	-	-
Quail	Japanese	0.22	0.22	0.22	0.22

Source: NRC (1994)

Maximum tolerable limits

The NRC (2005) defines the maximum tolerable level as the concentration "...of a mineral is the dietary level that, when fed for a defined period of time, will not impair animal health and performance." The NRC (2005) has set the following maximum tolerable levels for selenium in bird diets: a) 3 mg/kg for poultry and b) 2 mg/kg-dw for aquatic birds. Poultry includes chickens, turkeys, grouse, and pheasants, as well as ducks and geese (which are water birds). It should also be noted that the studies on kestrels did not produce adverse effects at up to 12 mg/kg-dw (Santolo et al. 1999, Yamamoto et al. 1998, Yamamoto and Santolo 2000).

Additional considerations

Issues to be considered in the collection and interpretation of samples include:

- tissue concentrations in fishes may vary with the time of year sampled
- tissue concentrations may vary by geographic location
- if sampling dietary items of birds, selenium concentrations may also differ among their prey items
- number of samples to collect
- the frequency of collections
- whether samples should be composited
- how to compare measured concentrations to screening values

These issues are discussed in greater detail in Section 6.

A point worthy of consideration is whether the type of food consumed affects the bioavailability and/or toxicity of selenium. The bird toxicity studies reviewed above would likely have used a feed that mainly consisted of cereal grains and oilseed meals (NRC 1994), whereas many of the bird species of concern in the North Bay are at least partially carnivorous. Among pigs, "*animal Se sources generally have a lower (<25%) absorption rate than Se from plant tissue. However, Se absorption is influenced by the type of animal product being fed. For example, the absorption of Se from bovine milk is high and equivalent to that of selenite, whereas Se in meat and bone meal or poultry by-products is ≤20%*" (Mahan 2001). This implies that the bioavailability of selenium is likely to be lower in the diets of the birds in the North Bay than in the diets used in the toxicity studies reviewed here. Thus, dietary screening levels for selenium may need to be adjusted upwards when they are based on studies where the test animal was fed mainly vegetable matter.

The toxicity values presented above were not derived using the populations and species of birds that occur in the North Bay nor using the environmental conditions in the North Bay. This means that there is some uncertainty as to whether any screening criteria are actually applicable. Similarly, McDonald and Chapman (2007) recommend that screening values only be used to determine if further evaluation is necessary. They recommend that if sample

concentrations exceed an appropriate screening value that actual impacts on the species of concern be assessed. Since reproductive success is the most sensitive endpoint in birds, it may be relatively easy to determine whether reproductive success of aquatic birds is being adversely impacted in the North Bay. This would require that an egg monitoring program be designed and implemented.

Future research and data gaps

Several data gaps and areas where further research may be beneficial to the Water Board were identified during the evaluation of selenium toxicity to birds in the North Bay, as follows:

1. The logistic regressions developed by the State of Utah (Ohlendorf 2007) to derive a dietary effect threshold for selenium should be redone using the correct data.
2. Toxicity studies have not been performed on most of the species of concern in the North Bay (USFWS 2007). Thus, this report has assumed that toxicity studies on mallards, chickens, pheasants, and screech owls are representative of the species of concern. The species of concern may be more or less sensitive.
3. If toxicity testing is not performed for the species of concern in the North Bay, another approach may be to develop selenium-specific allometric scaling factors for organic selenium in avian diets.
4. Species-specific regressions to convert dietary selenium concentrations to egg concentrations are lacking. If the Water Board decides to use the protection of egg hatching as a numeric criterion, this will be an important data gap.
5. The selenium toxicity studies performed to date have used selenite, selenomethionine, and selenized yeast. The degree to which the dietary formulations used in the toxicity studies reflects the speciation of selenium speciation in the food of birds of concern in the North Bay is not very well known. Since the speciation of selenium affects its toxicity, this may be an important consideration.
6. Toxicity experiments are uneven in assaying the actual amount of selenium in the experimental feeds. Many studies only report the estimated concentration added. Thus, the reported amount of selenium provided to birds in selenium toxicity studies is subject to some error. The error can be either positive or negative, depending upon the individual treatment.
7. Many toxicity studies performed to date report their concentration data in wet weight and do not provide a %moisture. Although a default %moisture can be used to estimate dry weight concentrations, this adds an additional layer of uncertainty as the actual %moisture will vary from sample to sample, at the very least.
8. A detailed re-analysis of the published toxicity data using, for example, biphasic regressions (Beckon 2007, Beckon et al. 2008) would provide a greater level of confidence in estimates of the threshold for toxic effects of selenium vs. a LOAEL, NOAEL, or effect threshold. However, if only the treatment means are available for the analyses, it should be remembered that this type of analysis will mask the true variability in the data.

4.5 CONCLUSIONS

Exposure to elevated levels of selenium can cause adverse effects in birds. Raptors, such as screech owls and kestrels, appear to be less sensitive to dietary exposures to selenium than ducks and chickens. While it has generally been recognized that reproductive success is the most sensitive endpoint in mallards, a review of the toxicity data available for chickens indicates that the growth/survival of young is a more sensitive endpoint in chickens. Thus, it is an open question as to which endpoint will be more sensitive for the birds of concern in the North Bay.

Numerous selenium screening values protective of birds have been proposed. For dietary selenium, the recommended screening values are usually in the range of 3-5 mg/kg-dw. For bird eggs, the range of recommended screening values is considerably larger, ranging from 6 to 74 mg/kg-dw.

Based upon the data presented here, there are several options for selenium screening values protective of birds. Those options are as presented below (all in units of mg/kg-dw). All of the screening values are well above the dietary requirements for birds of approximately 0.2 mg/kg-dw (Table 4-10), with the exception of some of the allometrically adjusted dietary thresholds, which are close to the dietary requirements.

1. The lowest dietary SMCV of 2.9 (Table 4-7)
2. Lowest dietary concentration at which adverse effects were reported (Table 4-7)
 - a. LOAEL of 4.3
3. The effect concentrations protective of reproductive success in mallards derived by the State of Utah (Ohlendorf 2007):
 - a. Dietary selenium
 - i. Logistic regression: 5.4
 - ii. Hockey stick-regression: 4.4
 - b. Egg selenium
 - i. Logistic regression: 12.5
 - ii. Hockey stick-regression: 11.5
4. Allometrically adjusted dietary thresholds for the species of concern in the North Bay (Table 4-9)
 - a. Note that allometric adjustment predicts that smaller birds will have lower dietary thresholds, with the lowest being approximately 1 mg/kg-dw for California clapper rails

The choice of using an SMCV, LOAEL, effect threshold, an EC01, or an EC10 is dependent upon both the level of risk and uncertainty the Water Board wishes to accept. This issue was presented in more detail in the Introduction. It is worth noting that of these values, only the LOAEL represents concentrations at which effects have been demonstrated. However, since only a few concentrations have been tested, effects may actually occur at lower concentrations.

5 MARINE MAMMAL TOXICITY REVIEW

Although some whale and dolphin species may occasionally enter the waters of the North Bay, they are generally considered infrequent visitors. The three marine mammal species that are considered to be resident in the North Bay include (DFG 2007, USFWS 1992):

- River otter (*Lontra canadensis*)
- Harbor seal (*Phoca vitulina*)
- California sea lion (*Zalophus californianus*)

Radio telemetry data indicates that harbor seals and sea lions venture in and out of the North Bay (USFWS 1992). None of the three marine mammal species found in the North Bay are special status species.

Among mammals exposure to elevated levels of selenium can cause reduced growth, emaciation, hair loss, lesions, paralysis, reduced conception rates, reduced litter size, increased stillbirths, and mortality (Mahan 2001, NRC 1980, 2005, Ohlendorf 2003). When selenium concentrations are high enough in a large enough area, these effects can lead to population declines for the most affected species.

The step in the effort to determine whether marine mammals may be adversely impacted by selenium in the North Bay is to evaluate the toxicity of selenium to the marine mammals. Next, potential selenium screening values for the species in the North Bay are proposed. Lastly, the screening values are compared to nutritional requirements.

5.1 METHODS

No toxicity studies have been performed on the effects of selenium on any marine mammal. Among mammals, selenium toxicity studies have been performed on cows, dogs, goats, hamsters, mice, pigs, and rats. However, “*due to the reduction of selenite and selenate, and the formation of insoluble particles in the rumen, cattle and sheep have [a] lower absorption of selenium... than non-ruminant species*” (NRC 2005). Therefore, toxicity studies where selenium has been fed to cows, sheep, and goats are probably not representative of marine mammals. Herbivorous and semi-herbivorous rodents (e.g., hamsters, mice, and rats) have reducing conditions in their intestines (as opposed to the stomach of ruminants) and also engage in coprophagy. Therefore, dietary toxicity studies on hamsters, mice, and rats are not likely to be reflective of carnivores, including marine mammals. Thus, it was assumed that dietary toxicity studies on pigs and dogs are likely to be representative of marine mammals.

Dietary selenium toxicity studies using pigs have been reviewed by the NRC (1980, 2005) and Mahan (2001). Studies on dogs have also been reviewed by the NRC (1980). The studies included in those reviews are summarized below in the Results section.

5.2 RESULTS

As stated above, no selenium toxicity studies on marine mammals were found. However, it was assumed that dietary toxicity studies on pigs and dogs are representative of marine

mammals as all three groups are carnivorous mammals. The studies on pigs and dogs reviewed by the NRC (1980, 2005) are provided in Tables 5-1 and 5-2 below, respectively.

Table 5-1
Dietary toxicity studies on pigs from NRC (1980, 2005).

Age	Chemical Form	Concentration (mg/kg)		Effect	Reference
		NOAEL	LOAEL		
"growing"	Na ₂ SeO ₃	4	8	reduced weight gain	Goehring et al. (1984)
"growing"	Na ₂ SeO ₃	5	15	reduced weight gain	Mahan and Magee (1991)
8-10 wk	Na ₂ SeO ₃ and SeMet	0.4	25	reduced weight gain, paralysis	Panter et al. (1996)
24.7 kg	Na ₂ SeO ₃ or Se-yeast	5	10	reduced weight gain	Kim and Mahan (2001a)
Adult	Na ₂ SeO ₃	4	8	offspring with reduced weight	Poulsen et al. (1989)
25 kg	Na ₂ SeO ₃ or Se-yeast	3	7	lower number of live born	Kim and Mahan (2001b)
5 kg	Na ₂ SeO ₃ and SeMet	10	20	reduced weight gain	Herigstad et al. (1973)
35 kg	Seleniferous corn	5	10	toxicosis	Schoening (1936)
15 kg	Na ₂ SeO ₃	-	7	reduced weight gain	Wahlstrom et al. (1956)
14 kg	Na ₂ SeO ₃	-	10	reduced weight gain	Wahlstrom et al. (1956)
13 kg	Na ₂ SeO ₃	-	11	reduced weight gain	Wahlstrom et al. (1956)
15 kg	Na ₂ SeO ₃	-	10	reduced reproductive success	Wahlstrom and Olson (1959)
16-19 kg	Na ₂ SeO ₃	-	24	Anorexia, death	Miller and Schoening (1938)

Table 5-2
Dietary toxicity studies on dogs from NRC (1980).

Age	Chemical Form	Concentration (mg/kg)		Effect	Reference
		NOAEL	LOAEL		
60 days	Seleniferous corn	-	7.2	Decreased weight gain	Rhian and Moxon (1943)
150 days	Na ₂ SeO ₃	-	10	Decreased weight gain	Rhian and Moxon (1943)
72 days	Seleniferous corn	-	20	Decreased weight gain	Rhian and Moxon (1943)
"young"	Na ₂ SeO ₃	-	20	Decreased weight gain	Moxon (1937)
"young"	Seleniferous corn	-	20	Decreased weight gain	Moxon (1937)

For all of the studies on presented above, it is unclear whether the dietary concentrations are provided as ww or dw. Thus, the units are given only as mg/kg.

Mahan (2001) summarizes the existing studies on pigs by stating that "chronic selenosis generally occurs when diets or feedstuffs contain 5 to 20 ppm Se."

5.3 DISCUSSION

No selenium toxicity studies have been performed on marine mammals. Therefore, it was assumed that toxicity studies on other mammals would be representative of marine mammals. Among the mammals that have been studied, it was assumed that pigs and dogs are more likely to be representative of the marine mammals of concern in the North Bay than studies using ruminants and rodents. This is because ruminants and rodents have reducing conditions in their gastro-intestinal tracts that may reduce the bioavailability of selenium relative to the gastrointestinal tracts of pigs, dogs, seals, sea lions, and otters.

The studies reviewed by the NRC (1980, 2005) indicate that effects in pigs were not observed at dietary concentrations of less than 7 mg/kg (Table 5-1). In *Nutrient Requirements of Swine* (NRC 1998), a study that was not reviewed in the *Mineral Tolerance of Animals* (NRC 1980, 2005) was cited as causing adverse effects in pigs at 5 mg/kg. Mahan (2001) also states that effects have been observed in pigs at feed concentrations at 5 mg/kg. Thus, it appears that the lowest reported dietary concentration at which selenium has been shown to affect pigs is approximately 5 mg/kg.

The studies reviewed by the NRC (1980) on dogs did not administer dietary concentrations below 7.2 mg/kg. Since adverse effects were observed at that dietary concentration, it is not possible to determine the actual effect threshold in dogs.

A point worthy of consideration is whether the type of food consumed affects the bioavailability and/or toxicity of selenium. The pig studies reviewed above would likely have used a feed that mainly consisted of corn and soybeans (NRC 1998), whereas seals, sea lions, and river otters are entirely carnivorous. Among pigs, “animal Se sources generally have a lower (<25%) absorption rate than Se from plant tissue. However, Se absorption is influenced by the type of animal product being fed. For example, the absorption of Se from bovine milk is high and equivalent to that of selenite, whereas Se in meat and bone meal or poultry by-products is ≤20%” (Mahan 2001). This implies that the bioavailability of selenium is likely to be lower in the diets of marine mammals than pigs and that the dietary screening level for selenium may need to be adjusted upwards of 5 mg/kg for marine mammals.

Allowable limits in feed

“In 1982, the FDA approved the addition of 0.3 ppm of selenium to diets for pigs up to 20 kg, because 0.1 ppm of added selenium does not always prevent deficiency signs in weanling pigs. The current regulation allows up to 0.3 ppm of selenium in the diet for all pigs” (NRC 1998).

Nutritional requirements

It should also be remembered that selenium is a micro-nutrient. When mammals do not have enough selenium in their diet, selenium deficiency results; i.e., edema, hepatic necrosis, poor growth, white muscle disease, mulberry heart disease, impaired reproduction, reduced milk production, impaired immune response, and mortality (NRC 1998). Due to the economic importance of the pig farming industry, the nutritional requirements to maintain an adequate growth rate and normal metabolism of pigs have been established by the NRC (1998; see Table 5-3 below) and Mahan (2001).

Table 5-3
Selenium nutritional requirements for commercially reared pigs (mg/kg-dw) by body weight (kg).

Body weight (kg)	NRC (1998)				Mahan (2001)			
	3-10	10-20	20-120	125+	5-20	20-60	60+	-
growing pigs	0.33	0.28	0.17		0.30	0.20	0.15	
gestating female				0.17				0.3
lactating female				0.17				0.3
Sexually active boars				0.17				

Maximum tolerable limits

The NRC (2005) defines the maximum tolerable level as the concentration "...of a mineral is the dietary level that, when fed for a defined period of time, will not impair animal health and performance." The NRC (2005) has set a maximum tolerable level of selenium in feed for pigs of 4 mg/kg (wet weight vs. dry weight not specified). The NRC (1998) also provides the following discussion of the maximum tolerable limit for selenium in pig feed:

"When fed to growing swine as sodium selenite, sodium selenate, selenomethionine, or seleniferous corn, selenium does not produce toxicity at levels of less than 5 ppm. In some cases, however, a level of 5 ppm and levels from 7.5 to 10 ppm have produced toxicity. Signs of toxicity include anorexia, hair loss, fatty infiltration of the liver, degenerative changes in the liver and kidney, edema, occasional separation of hoof and skin at the coronary band, and symmetrical, focal areas of vacuolation and neuronal necrosis."

Future research and data gaps

Several data gaps and areas where further research may be beneficial to the Water Board were identified during the evaluation of selenium toxicity to marine mammals in the North Bay, as follows:

1. Toxicity studies have not been performed on any of the marine mammals that reside in the North Bay. Thus, this report has assumed that toxicity studies on pigs and dogs are representative of harbor seals, sea lions, and river otters. The marine mammals in the North Bay may be more or less sensitive than pigs and dogs.
2. Toxicity studies on pigs have used a diet based on vegetable matter. The bioavailability of selenium in such diets is higher than in animal matter based diets. This means that the bioavailability of selenium in the diets of marine mammals may be lower than the in the toxicity studies that have been performed on pigs.
3. For this report, only the secondary literature was reviewed. A thorough examination of the primary literature (as was done for fish and birds) may prove more informative.
4. A detailed re-analysis of the published toxicity data for pigs using, for example, biphasic regressions (Beckon 2007, Beckon et al. 2008) would provide a greater level of confidence in estimates of the threshold for toxic effects of selenium vs. a LOAEL, NOAEL, or effect threshold. However, if only the treatment means are available for the analyses, it should be remembered that this type of analysis will mask the true variability in the data.
5. For harbor seals and sea lions, the collection and analysis of blood, hair, and blubber samples appears to be fairly routine. These types of samples can be collected without killing the seal/sea lion. It might prove useful to examine the dietary toxicity literature for pigs and develop relationships between dietary selenium levels and blood, fat, and/or hair levels in pigs that may be used to evaluate data collected from seals and sea lions in the North Bay.
6. The selenium toxicity studies performed to date have used selenite, selenomethionine, and selenized yeast. The degree to which the dietary formulations used in the toxicity studies reflects the speciation of selenium

speciation in the food of marine mammals of concern in the North Bay is not very well known. Since the speciation of selenium affects its toxicity, this may be an important consideration.

7. The secondary reviews do not detail whether the toxicity studies performed on pigs measured the selenium concentration in feed as ww or dw. This adds an additional layer of uncertainty.

5.4 CONCLUSIONS

Exposure to elevated levels of selenium can cause adverse effects in mammals. Based upon the data presented here, there are several options for selenium screening values protective of marine mammals. Those options are as follows (all in units of mg/kg):

1. The maximum tolerable limit recommended by that NRC (2005): 4
2. Lowest concentration at which adverse effects have been reported: 5

These proposed screening values are well in excess of the dietary requirements for pigs (which are assumed here to be representative of marine mammals) of approximately 0.3 mg/kg-dw (Table 5-3).

6 ISSUES AFFECTING THE CHOICE OF SCREENING VALUES

This report has presented several options for screening values protective of different receptor groups. Here, we discuss issues related to selecting a screening value for use in the TMDL process.

Derivation of screening values

In Section 1, multiple methods were identified that have been used in the toxicity literature to derive screening values, including:

- LOAELs
- Effect thresholds
- Species mean chronic values
- EC01 or EC10
- Species sensitivity distributions

Further, there are multiple means of calculating an effect concentrations (i.e., an EC01 or EC10) or a species sensitivity distribution. This means that different mathematical techniques can be applied to the same data to derive different screening values.

Determining which method is the best is no easy matter, as each method has its own limitations. Most of the selenium toxicity data examined in this review was collected from experiments designed to be analyzed using an ANOVA; i.e., there are several groups of animals in an experiment and each group is exposed to a different selenium dose. These types of experiments produce a NOAEL and a LOAEL; i.e., the highest selenium dose at which no adverse effects were observed and the lowest selenium dose at which adverse effects were observed.

Some authors have re-analyzed the treatment means from these kind of experiments using a regression analysis (e.g., logistic, hockey stick, or biphasic) to obtain a better understanding of the threshold for toxic effects than is provided by the NOAEL and LOAEL (e.g., Adams 2003, Ohlendorf 2003, 2007, Beckon 2007, 2008). However, in analyzing only the treatment means, significant variation is lost and the toxicity thresholds derived are uncertain.

Toxicity experiments designed to be analyzed using regression analyses have the potential to be much more powerful than toxicity tests designed to be analyzed using an ANOVA; i.e., “the purposes of accurately determining risk and maximizing benefit are more efficiently served by the allocation of limited experimental resources to a greater range of dose levels rather than to multiple replicates at a small number of dose levels. The latter, a legacy of traditional hypothesis testing, is relatively poorly suited for fitting and comparing mathematical models of the dose-response relationship” (Beckon et al. 2008). Therefore, it is recommended that future toxicity studies be designed with a regression analysis in mind.

When using an effect concentration (EC) or a species sensitivity distribution, one must also decide on what level to protect in order to derive the screening value. For effect thresholds, it is common to set the threshold at a 1, 10, or even 20% effect. For species sensitivity distributions, it is common to choose a value that is protective of 95% of the species evaluated. Choosing what threshold to use should be related to what level may actually impact populations in the field, yet information on that is scant. Further, when comparing screening values derived using either of these methods, one must also consider the confidence limits; e.g., is an EC10 of 1.8 significantly different from an EC20 of 2.5?

Uncertainties in toxicity testing

There are some additional sources of uncertainty associated with toxicological studies reviewed here that should be considered when interpreting the results to set regulatory standards, including the following:

- Responses to selenium differ among species and life-stage within the same species. However, results for one species of life-history stage are used to assess the effects on other species and life stages. For example, the only toxicity data available for white sturgeon were derived from short-term chronic (8-week) exposures to juvenile fish, but this fish is long-lived and does not reach sexual maturity until they are 10 years of age or more.
- In short-term toxicity tests performed on fish in the laboratory, the concentrations in the tissue may not have reached steady state. Thus, screening values derived from short term studies where tissue concentrations have not yet reached equilibrium may underestimate the tissue level that causes toxicity. However, current recommendations are to use fish tissue concentrations as screening values (Hamilton 2002, 2003, 2004, USEPA 2004).
- There is a lack of data linking the results of laboratory toxicity data to selenium concentrations and effects observed in the field. Even though effects have been demonstrated in the laboratory, it is unknown whether these effects will translate to population level effects in the field; i.e., population declines.

Current selenium toxicity testing efforts

At a recent meeting of the North American Industry Selenium Working Group (November 16, 2007) several new selenium toxicity studies were announced. These studies include the following:

- J.R. Simplot will spend approximately \$500K for selenium toxicity testing with brown trout, Yellowstone cutthroat trout, and possibly a third species.
- USEPA has performed a repeat of the bluegill toxicity test done by Lemly (1993a) upon which the USEPA (2004) based its draft ambient water quality criterion. Toxicity was found at higher concentrations than observed by Lemly (1993a). These results have not yet been published.

- The North American Industry Selenium Working Group may be funding relatively small studies on “site-specific assessments of selenium bioaccumulation in aquatic systems” and “tissue endpoint assessment.” However, the details of these studies are unknown.
- Cameco is performing “water bird research in Saskatchewan including assessing food, productivity, and egg [Se] for tree swallows.”

The research that is currently in progress described above is all on freshwater ecosystems. So, although the research is of general interest, it will not address the issues of greatest concern to the Board; i. e., the toxicity of selenium of brackish/marine ecosystems and the toxicity of selenium to the species of concern in the North Bay. Further, the current research does not appear to have been designed for use with regression analyses, meaning the NOAELs and LOAELs will be provided and deriving an EC20 will still be associated with some uncertainty.

Conclusions

Ultimately, given importance of selenium to the water resources of California, and the history of its effects, it is surprising that so little toxicity data on the species of concern in California is available. The methods used in selenium toxicity testing to date do not provide regulatory entities with a high degree of confidence in deriving toxicity thresholds and/or screening values. Lastly, field validation of selenium toxicity studies should also be performed to increase confidence in any screening levels derived from the existing toxicity literature.

7 ISSUES AFFECTING IMPLEMENTATION

When sampling invertebrates, fish, bird eggs, or other biological media to compare to the selenium screening values proposed in the earlier sections of this report, there are several issues that should be considered to maximize the use of the data. This section of the report provides a brief discussion of some of the more important issues. Some of these issues have been considered by various authors (e.g., Lemly and Skorupa 2007, McDonald and Chapman 2007, USEPA 2000, 2006).

Spatial variability

The concentration of selenium in the waters of the North Bay is expected to differ depending upon where samples are collected. Near selenium inputs (e.g., refineries, some creeks, and the San Joaquin River), selenium concentration in the water column are expected to be higher. This should result in higher concentrations for the biota that inhabit that area, providing that they have a relatively small range. For example, a clam may move only a few feet within its lifetime, but a sea lion may travel thousands of miles. Therefore, if there is an area where there is a localized input of selenium, elevated selenium levels would be expected in biota with a small range (e.g., the clam) but not necessarily in biota with a large range (e.g., the sea lion). This suggests that samples should be collected from areas near known selenium inputs from biota that are most likely to be impacted. To determine the extent of impacts, a number of locations should be sampled, not just areas near selenium inputs.

Background

Since selenium is a naturally occurring element, it is expected to be present at some concentration in all waters, soils, and sediments in the North Bay. Therefore, in addition to examining the spatial variability of selenium in the North Bay, it may be desirable to establish an area (or areas) that are representative of unimpacted (or reference) conditions. Then, biota may be sampled from that area and selenium concentrations in the tissues of biota from the background location can be compared to the samples collected from the North Bay to determine what areas are impacted. If this technique is used, it is advised that statistically robust techniques be used to compare sample locations, such as the t-test, ANOVA, or Kruskal-Wallis test.

Temporal variability

Concentrations of selenium in tissues may vary with the time of year. USEPA (2006) recommends that fish samples be collected during the same time of year during each sample event to avoid potential temporal effect.

Comparing measured concentrations to screening values

USEPA (2006) "... recommends using the [one sample] t-test to determine whether the mean concentration of mercury in composite fish tissue samples exceeds the screening value. This involves a statistical comparison of the mean of all fish tissue data to the criterion. EPA recommends that this procedure also be used for determining impairment." This technique is also applicable to selenium (without the compositing). To use a one-sample t-test, the screening value is compared against the mean concentration for all of the biota samples of the same species collected from the location/time being evaluated. The

results of the test can be used to determine whether the measured concentrations significantly exceed the screening value or not.

Another approach that can also be used is to compare the 95% upper confidence limit on the mean (UCL₉₅) to the screening value. If the calculated UCL₉₅ does not exceed the screening value, then no action is necessary. USEPA (2007b) provides free statistical software that can be used to calculate a UCL₉₅s for selenium data in biological samples.

Lastly, it is also possible to simply compare measured concentrations to the screening values. This method is likely to result in more exceedances than using a one sample t-test or a UCL₉₅. In that respect, comparing individual concentrations to the screening value may be more “sensitive” but it is not statistically valid.

Food webs

It has been demonstrated that among the fish species in the North Bay that those that feed on clams, or are part of a food web that starts with clams, have higher selenium tissue concentrations (Stewart et al. 2004). This is because the concentrations of selenium in one of the more abundant clams in the North Bay, *Potamocorbicula amurensis*, are much higher than many of the other invertebrates that fish feed on (Stewart et al. 2004). Similarly, it would be expected that birds that feed on this species of clam have higher selenium exposures than other bird species. In addition, it is generally expected that fish and birds that feed on biota in the sediments of the Bay would have greater selenium exposures than fish and birds that feed in the open water column; i.e., the Delta smelt only feed on zooplankton near the top of the water column and would, therefore, be expected to be exposed to less selenium than fish that feed in the sediments, such as sturgeon. However, it is possible that species that have a lower potential for exposure may be more sensitive to selenium. Thus, the other species in the North Bay should not be ignored.

Size of specimens

Data collected by the USGS indicate that as the size of Sacramento splittail increases over their lifetime, the fish's dietary habits change and that this affects their bioaccumulation of selenium. In addition, the concentrations of many metals increase with the size of the specimen sampled. For selenium, this does not always appear to be the case, but the potential effect of body size should be accounted for when collecting biota samples. Thus, body size (i.e., length and weight) should always be measured and data should be corrected for any relationship with size/weight (Tremblay et al. 1998, Wente 2004).

Frequency of collection

USEPA (2006) recommends that fish samples be collected at least once every two years to determine compliance with the fish tissue criterion for methylmercury. If a monitoring strategy for the North Bay is implemented, it may be appropriate to collect samples annually, at least initially.

Compositing

When collecting fish samples to support fish consumption advisories, USEPA (2000, 2006) recommends the collection of composite samples. What this means is that samples are collected from several fish individuals, but then the samples are homogenized and the laboratory analyzes only the single composite sample. This approach is designed to

minimize costs and to provide an indication of the average concentration. However, compositing biota samples makes evaluating relationships between 1) age, sex, size, time of year and 2) selenium concentration more difficult. Further, the costs for low level selenium analyses in tissues have fallen in recent years. Therefore, it is recommended that biota samples should not be composited, at least for organisms where it is possible to obtain samples large enough for analysis from a single individual (i.e., 2 g).

Sample size

If the Water Board elects to use the statistical techniques recommended above, then it is recommended that a minimum of eight samples be collected for a species during each sampling event. This will provide the necessary sample size to perform both background comparisons and the calculation of a UCL₉₅. This is consistent with USEPA (2007b) recommendations.

Fish tissue screening value protective of human health

The State of California (OEHHA 2006) has calculated a screening value for selenium in fish tissue that is protective of fishermen (i.e., the human consumption fish). The screening value was calculated using toxicity data from USEPA (2007c). It should be noted that the calculations that the State of California (OEHHA 2006) used assume a 100% bioavailability of selenium in fish tissues to humans. However, as stated in the section on the toxicity of selenium to marine mammals, the bioavailability of selenium in animal tissues is generally lower (<25%) (Mahan 2001). This may need to be evaluated in more detail prior to implementing the fish tissue screening value protective of human health in the North Bay.

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APPENDIX A

WET WEIGHT TO DRY WEIGHT CONVERSIONS

Concentrations of selenium in tissues and animal feed are reported in either wet weight (ww) or dry weight (dw). Unfortunately, the two measurements are not equivalent. The selenium concentrations that were used in the analyses presented earlier in this report are presented in their original units in Table A-1. All of the selenium concentrations reported in Table A-1 were converted to dry weight using either the percent moisture reported in the original publication or the default percent moisture of 75% (USEPA 1993) for studies on fish where the percent moisture was not reported. The percent moisture used in the calculations is presented in Table A-1 and the dry weight selenium concentrations are reported in Table A-2. The formula used to convert wet weight to dry weight is as follows:

$$\text{Dry weight} = \text{wet weight} \times \frac{100}{100 - \text{percent moisture}}$$

Additionally, not all studies measured selenium in all tissue types. USEPA (2004) provides equations to convert selenium concentrations in fish muscle and liver to whole body concentrations. The data that USEPA (2004) presented was also used to derive linear regression equations to convert selenium concentrations measured in one tissue type to another tissue type for all fish, except white sturgeon. The equations used are provided below and are given in order of preference used to estimate tissue concentrations.

1. Selenium in fish muscles to whole body (USEPA 2004):

$$Se_{\text{wholebody}} = \exp[0.1331 + (0.8937 \times \ln(Se_{\text{muscle}}))]$$

2. Selenium in fish liver to whole body (USEPA 2004):

$$Se_{\text{wholebody}} = -0.2609 + (0.3071 \times Se_{\text{liver}})$$

3. Selenium in whole fish bodies to fish livers ($p < 0.0001$, $r^2 = 0.73$):

$$Se_{\text{liver}} = \exp[1.6475 + (0.7628 \times \ln(Se_{\text{wholebody}}))]$$

4. Selenium in whole fish bodies to fish muscle ($p < 0.0001$, $r^2 = 0.96$):

$$Se_{\text{muscle}} = \exp[0.0324 + (1.031 \times \ln(Se_{\text{wholebody}}))]$$

For white sturgeon, TetraTech obtained the raw data from the study conducted by Tashjian et al. (2006) and used that data to calculate the following regression equation ($F_{1,22} = 222.42$, Adjusted $R^2 = 0.91$, $p < 0.00001$):

$$Se_{\text{wholebody}} = \exp[0.9586 + (0.6206 \times \ln(Se_{\text{muscle}}))]$$

This regression equation was used to convert the muscle EC10 derived by Beckon to a whole body concentration as well as the muscle NOAEL and LOAEL from Linville (2006) to whole body concentrations.

For the selenium toxicity studies on birds, only the concentration in the feed given to the birds was converted from wet weight to dry weight. That is presented in Table A-4 for toxicity studies and A-5 for production studies.

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Table A-1
Fish Tissue Concentration Data
Measured Selenium Concentrations (mg/kg or ug/g)

Fish	Study	Water		Exposure Route	Kidney Se (mg/kg)		Liver Se (mg/kg)		Muscle Se (mg/kg)		Whole Body Se (mg/kg)		dw/ww	%moisture ¹	Notes	Effect		Used in
		Type	Life stage		NOAEL	LOAEL	NOAEL	LOAEL	NOAEL	LOAEL	NOAEL	LOAEL				Major	Minor	
Bluegill	Cleveland (1993)	fresh	Juvenile	Water	-	-	-	-	-	-	3.0	3.4	dw	-	2	X		
Bluegill	Cleveland (1993)	fresh	Juvenile	Diet	-	-	-	-	-	-	4.7	7.6	dw	-	2	X	X	
Bluegill	Coyle et al. (1993)	fresh	Adult	Water/Diet	-	-	-	-	-	-	10	19	dw	-	2,4	X	X	
Bluegill	Coyle et al. (1993)	fresh	egg	Water/Diet	-	-	-	-	-	-	23	41	dw	-	2,4	X		
Bluegill	Doroshov et al. (1992)	fresh	Adult	Diet	-	-	12.3	26.0	5.8	10.4	-	-	dw	-	-	X	X	
Bluegill	Finley (1985)	fresh	adult	Diet	-	-	5.0	8.5	2.06	5.10	-	-	ww	75	-	X		
Bluegill	Gillespie and Baumann (1986)	fresh	Fry/larvae	Natural	-	-	-	-	-	-	3.1	28.2	dw	-	-	X		
Bluegill	Gillespie and Baumann (1986)	fresh	Adult	Natural	-	-	-	-	-	-	0.4	5.9	ww	75	-	X		
Bluegill	Hermanutz et al. (1992)	fresh	adult	Water/Diet	-	-	1.5	9.3	0.3	1.8	-	-	ww	75	-	X	X	
Bluegill	Lemly (1993a); Skorupa et al. 2004	fresh	Juvenile	Water/Diet	-	-	-	-	-	-	1.3	5.8	dw	-	-	X	X	
Bluegill	Sorensen et al. (1984)	fresh	Adult	Natural	-	-	1.3	7.0	1.3	2.3	-	-	ww	75	-	X		
channel catfish	Doroshov et al. (1992)	fresh	Adult	Injection	-	-	7.3	12.5	-	-	-	-	dw	-	-			
channel catfish	Gatlin and Wilson (1984)	fresh	fingerling	Diet	-	-	-	-	3.0	3.5	-	-	dw	-	-	X	X	
chinook salmon	Hamilton et al. (1990)	fresh	larvae	Diet	-	-	-	-	-	-	5.4	10.8	dw	-	6	X	X	
chinook salmon	Hamilton et al. (1990)	brackish	juvenile	Diet	-	-	-	-	-	-	12.6	23.2	dw	-	6	X	X	
fathead minnow	Dobbs et al. (1996)	fresh	larvae	Water/Diet	-	-	-	-	-	-	-	62	dw	-	-	X	X	
fathead minnow	Ogle and Knight (1989)	fresh	juvenile	Diet	-	-	-	-	5.7	6.6	5.4	6.6	dw	-	-	X	X	
fathead minnow	Schultz and Hermanutz (1990)	fresh	egg	Water/Diet	-	-	-	-	-	-	0.3	3.9	ww	80	-	X	X	
green sunfish	Lemly (1993b)	fresh	Adult	Natural	-	-	-	-	-	-	12.4	14.7	dw	-	-	X		
rainbow trout	Hicks et al (1984)	fresh	juvenile	Diet	3.0	10.7	38.3	49.3	-	-	-	-	ww	75	-	X	X	
rainbow trout	Hilton and Hodson (1983)	fresh	juvenile	Diet	0.7	3.8	0.6	21.0	-	-	0.2	1.0	dw	-	3, 4		X	
rainbow trout	Hilton and Hodson (1983)	fresh	juvenile	Diet	3.8	7.7	21.0	71.7	-	-	1.0	4.0	dw	-	3, 4	X	X	
rainbow trout	Hilton et al. (1980)	fresh	juvenile	Water/Diet	9	37	42.0	95.0	-	-	-	-	dw	-	2	X	X	
rainbow trout	Holm et al. (2005)	fresh	adult	Natural	-	-	-	-	-	1.8	-	-	ww	75	-	X		
rainbow trout	Holm et al. (2005)	fresh	egg	Natural	-	-	-	-	-	-	-	3.5	ww	61	-	X		
rainbow trout	Hunn et al (1987)	fresh	Fry/larvae	Water	-	-	-	-	-	-	0.5	0.9	dw	-	4		X	
rainbow trout	Hunn et al (1987)	fresh	Fry/larvae	Water	-	-	-	-	-	-	0.6	1	dw	-	4	X		
rainbow trout	Vidal et al (2005)	fresh	Fry/larvae	Diet	-	-	-	-	-	-	0.3	0.6	ww	75	-	X	X	
Redear sunfish	Sorensen et al. (1988)	fresh	Adult	Natural	2.1	7.6	-	-	0.3	5.0	-	-	ww	75	5	X		
Sacramento splittail	Teh et al. (2004)	fresh	juvenile	Diet	-	-	23.0	26.8	10.1	15.1	-	-	dw	-	-	X	X	
Striped Bass	Coughlan and Velte (1989)	fresh	Adult	Diet	-	-	-	-	1.1	3.5	-	-	ww	75	-	X		
white sturgeon	Linville (2006)	fresh	Adult	Diet	-	-	1.4	10.4	1.3	12.1	-	-	dw	-	-	X	X	
white sturgeon	Tashjian et al. (2006)	fresh	juvenile	Diet	30.9	51.7	22.0	37.4	22.9	36.8	14.7	22.5	dw	-	-	X	X	

Notes:

- 1 - a value of 75% is the default assumption (USEPA 19930)
- 2 - concentration estimated from figures
- 3 - data from the low carbohydrate diet were not used as the authors reported that reduced weight of fish on this diet was likely due to food
- 4 - dry weight assumed. Not explicitly stated whether dw or ww
- 5 - muscle concentration calculated using regression equation from Sorensen et al. (1982); i.e., muscle concentration = kidney concentration x 0.835 - 1.375
- 6 - excludes treatment where fish were exposed to water from the San Luis Drain

Table A-2
Wet Weight to Dry Weight Conversion for Fish Tissue Concentration Data
Selenium Concentrations in Dry Weight (mg/kg-dw or ug/g-dw)

Fish	Study	Water		Exposure Route	Kidney Se (mg/kg)		Liver Se (mg/kg)		Muscle Se (mg/kg)		Whole Body Se (mg/kg)		Effect		Used in SMCV
		Type	Life stage		NOAEL	LOAEL	NOAEL	LOAEL	NOAEL	LOAEL	NOAEL	LOAEL	Major	Minor	
Bluegill	Cleveland (1993)	fresh	Juvenile	Water	-	-	-	-	-	-	3.0	3.4		X	
Bluegill	Cleveland (1993)	fresh	Juvenile	Diet	-	-	-	-	-	-	4.7	7.6	X		X
Bluegill	Coyle et al. (1993)	fresh	Adult	Water/Diet	-	-	-	-	-	-	10.0	19.0	X		X
Bluegill	Coyle et al. (1993)	fresh	egg	Water/Diet	-	-	-	-	-	-	23.0	41.0	X		
Bluegill	Doroshov et al. (1992)	fresh	Adult	Diet	-	-	12.3	26.0	5.8	10.4	-	-	X		X
Bluegill	Finley (1985)	fresh	adult	Diet	-	-	20.0	33.9	8.2	20.4	-	-	X		
Bluegill	Gillespie and Baumann (1986)	fresh	Fry/larvae	Natural	-	-	-	-	-	-	3.1	28.2	X		
Bluegill	Gillespie and Baumann (1986)	fresh	Adult	Natural	-	-	-	-	-	-	1.5	23.6	X		
Bluegill	Hermanutz et al. (1992)	fresh	adult	Water/Diet	-	-	6.0	37.2	1.2	7.2	-	-	X		X
Bluegill	Lemly (1993a); Skorupa et al. 2004	fresh	Juvenile	Water/Diet	-	-	-	-	-	-	1.3	5.8	X		X
Bluegill	Sorensen et al. (1984)	fresh	Adult	Natural	-	-	5.2	28.0	5.2	9.2	-	-	X		
channel catfish	Doroshov et al. (1992)	fresh	Adult	Injection	-	-	7.3	12.5	-	-	-	-	X		X
channel catfish	Gatlin and Wilson (1984)	fresh	fingerling	Diet	-	-	-	-	3.0	3.5	-	-	X		X
chinook salmon	Hamilton et al. (1990)	fresh	larvae	Diet	-	-	-	-	-	-	5.4	10.8	X		X
chinook salmon	Hamilton et al. (1990)	fresh	brackish	Diet	-	-	-	-	-	-	12.6	23.2	X		X
fathead minnow	Dobbs et al. (1996)	fresh	larvae	Water/Diet	-	-	-	-	-	-	-	62.0	X		X
fathead minnow	Ogle and Knight (1989)	fresh	juvenile	Diet	-	-	-	-	5.7	6.6	5.4	6.6	X		X
fathead minnow	Schultz and Hermanutz (1990)	fresh	egg	Water/Diet	-	-	-	-	-	-	1.6	19.6	X		X
green sunfish	Lemly (1993b)	fresh	Adult	Natural	-	-	-	-	-	-	12.4	14.7	X		
rainbow trout	Hicks et al (1984)	fresh	juvenile	Diet	12.0	42.8	153.2	197.2	-	-	-	-	X		X
rainbow trout	Hilton and Hodson (1983)	fresh	juvenile	Diet	0.7	3.8	0.6	21.0	-	-	0.2	1.0		X	
rainbow trout	Hilton and Hodson (1983)	fresh	juvenile	Diet	3.8	7.7	21.0	71.7	-	-	1.0	4.0	X		X
rainbow trout	Hilton et al. (1980)	fresh	juvenile	Water/Diet	9.0	37.0	42.0	95.0	-	-	-	-	X		X
rainbow trout	Holm et al. (2005)	fresh	adult	Natural	-	-	-	-	-	7.2	-	-	X		
rainbow trout	Holm et al. (2005)	fresh	egg	Natural	-	-	-	-	-	-	-	9.0	X		
rainbow trout	Hunn et al (1987)	fresh	Fry/larvae	Water	-	-	-	-	-	-	0.5	0.9		X	
rainbow trout	Hunn et al (1987)	fresh	Fry/larvae	Water	-	-	-	-	-	-	0.6	1.1	X		
rainbow trout	Vidal et al (2005)	fresh	Fry/larvae	Diet	-	-	-	-	-	-	1.2	2.3	X		X
Redear sunfish	Sorensen et al. (1988)	fresh	Adult	Natural	8.2	30.5	-	-	1.3	20.0	-	-	X		
Sacramento splittail	Teh et al. (2004)	fresh	juvenile	Diet	-	-	23.0	26.8	10.1	15.1	-	-	X		X
Striped Bass	Coughlan and Velte (1989)	fresh	Adult	Diet	-	-	-	-	4.4	14.0	-	-	X		
white sturgeon	Linville (2006)	fresh	Adult	Diet	-	-	1.4	10.4	1.3	12.1	-	-	X		X
white sturgeon	Tashjian et al. (2006)	fresh	juvenile	Diet	30.9	51.7	22.0	37.4	22.9	36.8	14.7	22.5	X		X

Table A-3
Conversion of Fish Tissue Concentration Data Among Tissue Types
Selenium Concentrations in Dry Weight (mg/kg-dw or ug/g-dw)

Fish	Study	Water		Exposure Route	Kidney Se (mg/kg)		Liver Se (mg/kg)		Muscle Se (mg/kg)		Whole Body Se (mg/kg)		Effect		Used in SMCV
		Type	Life stage		NOAEL	LOAEL	NOAEL	LOAEL	NOAEL	LOAEL	NOAEL	LOAEL	NOAEL	LOAEL	
Bluegill	Cleveland (1993)	fresh	Juvenile	Water	-	-	12.0	13.2	3.2	3.6	3.0	3.4			X
Bluegill	Cleveland (1993)	fresh	Juvenile	Diet	-	-	16.8	24.5	5.1	8.4	4.7	7.6	X		X
Bluegill	Coyle et al. (1993)	fresh	Adult	Water/Diet	-	-	30.1	49.1	11.1	21.5	10.0	19.0	X		X
Bluegill	Coyle et al. (1993)	fresh	egg	Water/Diet	-	-	-	-	-	-	23.0	41.0		X	
Bluegill	Doroshov et al. (1992)	fresh	Adult	Diet	-	-	12.3	26.0	5.8	10.4	5.5	9.3	X		X
Bluegill	Finley (1985)	fresh	adult	Diet	-	-	20.0	33.9	8.2	20.4	7.5	16.9	X		
Bluegill	Gillespie and Baumann (1986)	fresh	Fry/larvae	Natural	-	-	12.3	66.3	3.3	32.3	3.1	28.2	X		
Bluegill	Gillespie and Baumann (1986)	fresh	Adult	Natural	-	-	7.0	58.0	1.5	26.9	1.5	23.6		X	
Bluegill	Hermanutz et al. (1992)	fresh	adult	Water/Diet	-	-	6.0	37.2	1.2	7.2	1.3	6.7	X		X
Bluegill	Lemly (1993a); Skorupa et al. 2004	fresh	Juvenile	Water/Diet	-	-	6.3	19.9	1.4	6.3	1.3	5.8	X		X
Bluegill	Sorensen et al. (1984)	fresh	Adult	Natural	-	-	5.2	28.0	5.2	9.2	5.0	8.3	X		
channel catfish	Doroshov et al. (1992)	fresh	Adult	Injection	-	-	7.3	12.5	2.1	3.8	2.0	3.6	X		X
channel catfish	Gatlin and Wilson (1984)	fresh	fingerling	Diet	-	-	-	-	3.0	3.5	3.1	3.5	X		X
chinook salmon	Hamilton et al. (1990)	fresh	larvae	Diet	-	-	18.8	31.9	5.9	12.0	5.4	10.8	X		X
chinook salmon	Hamilton et al. (1990)	brackish	juvenile	Diet	-	-	35.9	57.2	14.1	26.4	12.6	23.2	X		X
fathead minnow	Dobbs et al. (1996)	fresh	larvae	Water/Diet	-	-	-	121.0	-	72.8	-	62.0	X		X
fathead minnow	Ogle and Knight (1989)	fresh	juvenile	Diet	-	-	18.8	21.9	5.7	6.6	5.4	6.6	X		X
fathead minnow	Schultz and Hermanutz (1990)	fresh	egg	Water/Diet	-	-	-	-	-	-	1.6	19.6	X		X
green sunfish	Lemly (1993b)	fresh	Adult	Natural	-	-	35.4	40.3	13.8	16.5	12.4	14.7	X		
rainbow trout	Hicks et al (1984)	fresh	juvenile	Diet	12.0	42.8	153.2	197.2	-	-	46.8	60.3	X		X
rainbow trout	Hilton and Hodson (1983)	fresh	juvenile	Diet	0.7	3.8	0.6	21.0	0.2	1.0	0.2	1.0	X		
rainbow trout	Hilton and Hodson (1983)	fresh	juvenile	Diet	3.8	7.7	21.0	71.7	1.0	4.3	1.0	4.0	X		X
rainbow trout	Hilton et al. (1980)	fresh	juvenile	Water/Diet	9.0	37.0	42.0	95.0	-	-	12.6	28.9	X		X
rainbow trout	Holm et al. (2005)	fresh	adult	Natural	-	-	-	-	-	7.2	-	6.7	X		
rainbow trout	Holm et al. (2005)	fresh	egg	Natural	-	-	-	-	-	-	-	9.0	X		
rainbow trout	Hunn et al (1987)	fresh	Fry/larvae	Water	-	-	3.2	4.7	0.5	0.9	0.5	0.9	X		
rainbow trout	Hunn et al (1987)	fresh	Fry/larvae	Water	-	-	3.7	5.5	0.7	1.1	0.6	1.1	X		
rainbow trout	Vidal et al (2005)	fresh	Fry/larvae	Diet	-	-	6.1	9.9	1.3	2.5	1.2	2.3	X		X
Redear sunfish	Sorensen et al. (1988)	fresh	Adult	Natural	8.2	30.5	-	-	1.3	20.0	1.5	16.6	X		
Sacramento splittail	Teh et al. (2004)	fresh	juvenile	Diet	-	-	23.0	26.8	10.1	15.1	9.0	12.9	X		X
Striped Bass	Coughlan and Velte (1989)	fresh	Adult	Diet	-	-	-	-	4.4	14.0	4.3	12.1	X		
white sturgeon	Linville (2006)	fresh	Adult	Diet	-	-	1.4	10.4	1.3	12.1	3.1	12.3	X		X
white sturgeon	Tashjian et al. (2006)	fresh	juvenile	Diet	30.9	51.7	22.0	37.4	22.9	36.8	14.7	22.5	X		X

Note: shaded cells represent predicted concentrations. See text for explanation.

Table A-4
Wet Weight to Dry Weight Conversion for Bird Dietary Concentration Data
Measured Selenium Concentrations (mg/kg or ug/g)

Bird	Study	Life stage	Chemical form	Measured Diet Se (mg/kg)				Diet Se (mg/kg-dw)		Effect	
				NOAEL	LOAEL	dw/ww	%moisture	NOAEL	LOAEL	Major	Minor
Chicken	Elzubier and Davis (1988)	Chick	selenite	0.15	10	?	?	0.15	10	X	
Chicken (Hubbard)	Jensen (1976)	Chick	selenite	0.9	4.3	dw	-	0.9	4.3	X	
Chicken (leghorn)	Jensen (1976)	Chick	selenite	4.3	13.5	dw	-	4.3	13.5	X	
Chicken	Lowry and Baker (1989)	Chick	selenite; SeMet	0	15	?	?	0	15	X	
Chicken	Ort and Latshaw (1978)	Adult	selenite	3	5	?	?	3	5	X	
Common eider	Franson et al. (2007)	Adult	SeMet	20.6	57.7	dw	-	20.6	57.7	X	
Mallard	Albers et al. (1996)	Adult	SeMet	20	40	ww	10.5	22.3	44.7	X	
Mallard	Green and Albers 1996	Adult	SeMet	10	20	ww	10.5	11.2	22.3	X	
Mallard	Heinz and Hoffman, 1998	Adult	SeMet	0.4	8.8	ww	10	0.4	9.8	X	
Mallard	Heinz et al., 1987	Adult	selenite	10	25	ww	8.5	10.9	27.3	X	
Mallard	Heinz et al., 1987	Adult	SeMet	0	10	ww	8.5	0.0	10.9	X	
Mallard	Heinz et al., 1988	Duckling	selenite	10.1	20.1	ww	7	10.9	21.6	X	
Mallard	Heinz et al., 1988	Duckling	SeMet	10.1	20.1	ww	7	10.9	21.6	X	
Mallard	Heinz et al., 1989	Adult	SeMet	4.1	8.1	ww	10	4.6	9.0	X	
Mallard	Heinz et al., 1989	Adult	SeCysteine	10.1	-	ww	10	11.2	-	X	
Mallard	Heinz et al. (1996)	Duckling	SeMet	15.34	30.34	ww ¹	10	17.0	33.7	X	
Mallard	Hoffman and Heinz (1998)	Adult	SeMet	0.4	10.4	ww	10	0.4	11.6		X
Mallard	Hoffman et al. (1991)	Duckling	SeMet; low protein	0.2	15.2	ww	10	0.2	16.9	X	
Mallard	Hoffman et al. (1991)	Duckling	SeMet	15.2	60.2	ww	10	16.9	66.9	X	
Mallard	Hoffman et al. (1992a)	Duckling	SeMet	0.2	15.2	ww	10	0.2	16.9	X	
Mallard	Hoffman et al., 1992b	Duckling	SeMet	0.2	15.2	ww	8	0.2	16.5		X
Mallard	Hoffman et al., 1992b	Duckling	SeMet	15.2	60.2	ww	8	16.5	65.4	X	
Mallard	Hoffman et al., 1992b	Duckling	SeMet; low protein	15.2	60.2	ww	8	16.5	65.4	X	
Mallard	Hoffman et al., 1992b	Duckling	SeMet; low protein	0.2	15.2	ww	8	0.2	16.5		X
Mallard	Hoffman et al., 1992b	Duckling	SeMet; high protein	0.2	15.2	ww	8	0.2	16.5	X	
Mallard	Hoffman et al. (1996)	Duckling	SeMet, Se yeast, Se in wheat	0.2	15.2	ww ¹	10	0.2	16.9		X
Mallard	O'Toole and Raisbeck (1997)	Flightling	SeMet	10.32	25.32	ww	25	13.8	33.8	X	
Mallard	Stanley et al. (1994)	Adult	SeMet	0.37	6.5	dw	-	0.37	6.5	X	
Mallard	Stanley et al. (1996)	Adult	SeMet	3.5	7	ww	10	3.9	7.8	X	
Pheasant	Latshaw et al. (2004)	Adult	unknown	-	9.3	dw	-	-	9.3	X	
Screech owl	Wiemeyer and Hoffman (1996)	Adult	SeMet	8.8	30	dw	-	8.8	30	X	
Screech owl	Wiemeyer and Hoffman (1996)	Adult	SeMet	0.3	8.8	dw	-	0.3	8.8		X

Notes: 1 - a %moisture of 10 was assumed based on other studies by the same authors where a %moisture was specified.

Table A-5
Summary of Chicken Enhanced Production Studies
Measured Selenium Concentrations (mg/kg or ug/g)

Bird	Study	Life stage	Dietary form	Measured NOAEL			NOAEL	Effects			
				(mg/kg)	dw/ww	%moisture	(mg/kg-dw)	Survival	Weight	Egg output	Reproductive success
Chicken	Payne et al. (2005)	Adult	selenite	2.6	?	-	2.6			X	
Chicken	Payne et al. (2005)	Adult	Se-yeast	2.9	?	-	2.9			X	
Chicken	Ryu et al. (2005)	1 day	selenite	8.2	dw	-	8.2		X		
Japanese quail	Biswas et al. (2006)	1 day	selenite	1.2	?	-	1.2	X	X		
Japanese quail	Sahin and Kucuk (2001)	10 day	selenite	0.2	ww	10.32	0.2		X		

APPENDIX B

THRESHOLD VALUES FOR SELENIUM IN GREAT SALT LAKE

Threshold Values for Selenium in Great Salt Lake: Selections by the Science Panel

PREPARED FOR: Great Salt Lake Science Panel

PREPARED BY: Harry Ohlendorf

COPIES: Jeff DenBleyker
Earl Byron
Gary Santolo
Dan Moore
Principal Investigators

DATE: February 28, 2007

PROJECT NUMBER: 341055.PP.QC

The purpose of this technical memorandum is to provide a summary and documentation of the Science Panel's discussions relative to toxicity thresholds for exposure of birds to selenium at the Great Salt Lake. It is generally recognized that the most significant exposure of birds occurs through their diet, and that the best-documented and most readily-monitored effects are those on reproductive success (particularly egg hatchability). Thus, much of the focus of this technical memorandum is on those exposures and endpoints, because they can be most readily applied toward establishment of a site-specific water quality standard for selenium in the open waters of the Great Salt Lake.

Before the Science Panel meeting on November 29-30, 2006, I prepared a technical memorandum (Subject: Threshold Values for Selenium in Great Salt Lake; dated November 28) to provide the following:

- a summary of potential threshold values identified by Science Panel members for consideration in establishing a water quality standard for selenium in the open waters of the Great Salt Lake, and
- supporting documentation and literature provided by Panel members to be used as the basis of discussion by the Panel.

Bill Adams, Anne Fairbrother, Theresa Presser, and Joe Skorupa provided input concerning threshold values to be considered and sent supporting literature (either as citations or copies of publications), in addition to providing their views on the threshold values themselves. The entire Panel discussed that material and related information from other sources on November 30. From the available information, the Panel narrowed the ranges of values for bird diets and eggs to those listed in Tables 1 and 2 (Attachment A [tables modified from the compilation of field and laboratory data presented in Table 15 of Presser and Luoma, 2006]) and then identified "working values" for the ranges of acceptable selenium concentrations in bird diets and in bird eggs (those shaded in the tables). It is understood that the values will likely be refined during future phases of work (including consideration of site-specific

data currently being generated by the Great Salt Lake research effort) and discussion related to establishing a site-specific standard for Great Salt Lake.

A previous draft of this technical memorandum (dated December 8) provided a brief summary of the threshold values that were selected by the Panel during those discussions. For both diet and eggs, the ranges of selenium concentrations selected by the Panel are the lower and upper 95 percent confidence intervals (95% CIs; also referred to as the 5 percent lower confidence limit [LCL] and the 95 percent upper confidence limit [UCL]) for the mean selenium concentration that is associated with a 10 percent reduction (i.e., the 10 percent effect concentration or EC_{10}) in the hatchability of mallard eggs. Those values were reported by Ohlendorf (2003), based on the analysis of data from six laboratory studies (Heinz et al. 1987, 1989; Heinz and Hoffman 1996, 1998; Stanley et al. 1994, 1996). Essentially, there is 95 percent confidence that the mean dietary or egg selenium concentration that causes a 10 percent reduction of egg hatchability is within the identified ranges, which are illustrated in the figures below.

The Panel agreed by consensus that the 95% CIs on mean selenium concentrations in mallard diet and eggs associated with the EC_{10} for egg hatchability would be reasonably protective for birds nesting at the Great Salt Lake, and that the ranges of values represented by the 95% CIs included the concentrations proposed by various Panel members for consideration. Rationale supporting selection of the 95% CIs is provided by the previous technical memorandum (dated November 28) and through discussion at the Panel meeting.

Panel members provided comments on the December 8 draft version of this technical memorandum summarizing threshold values (Attachment B), and Bill Adams provided further data analyses of effect levels in diets and eggs of mallards that are included in this revised draft. Additional considerations and qualifications about the selected dietary and egg concentrations are presented below in the Discussion section.

All concentrations in bird diets or eggs mentioned below are expressed on dry-weight basis.

Selenium in Bird Diets

The dietary selenium EC_{10} for mallards was reported as 4.87 mg/kg, with 95% CIs of 3.56 to 5.74 mg/kg based on reproductive toxicity (egg hatchability) (Ohlendorf 2003). The EC_{10} of 4.87 mg/kg was estimated by fitting a logistic regression model (Figure 1). It should be noted, however, that the mallard studies used a “dry diet” that had about 10 percent moisture. Ohlendorf (2003) used the reported dietary selenium concentrations without adjustment for that moisture content, but an upward adjustment of the values (by 11 percent) would be appropriate to account for the moisture content of the duck diet.

In Adams et al. (2003), hockey-stick regression was used to model relationships between egg selenium concentrations and adverse effects in order to derive toxicity thresholds, such as EC_{10} values. Hockey-stick regression is a model that has been used elsewhere to define a threshold when an underlying background level of response is unrelated to the dose (see Adams comments in Attachment B). Thus, such a model may be relevant to naturally occurring elements that are essential to birds and a wide variety of other organisms and particularly useful for elements such as selenium, which has a narrow range between levels that are essential and those that are toxic to birds so that variance around the inflection point (threshold) in the model is small. As shown in Figure 2 below, a threshold clearly

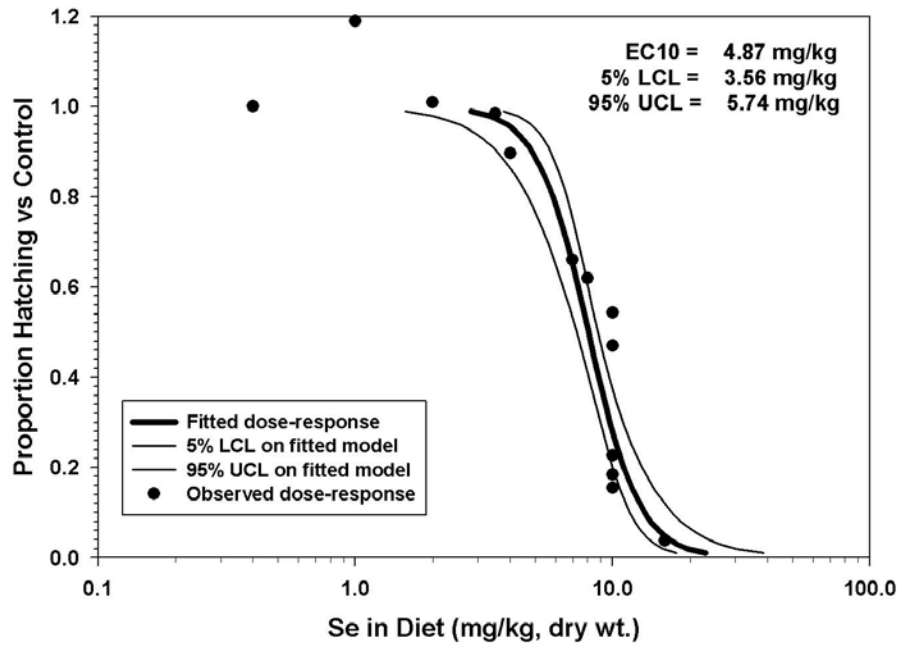


Figure 1. Mallard egg hatchability vs control as a function of selenium concentration in diet.

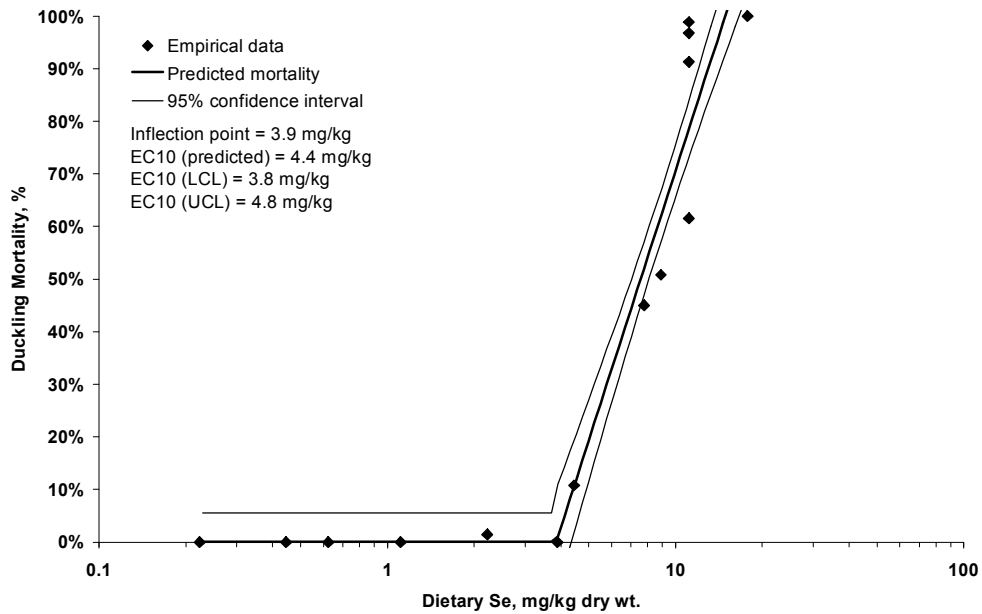


Figure 2. Hockey stick regression of laboratory mallard duckling mortality versus dietary selenium.

appears to exist when dietary selenium is plotted versus duckling mortality (which incorporated the cumulative effects of fertilization success and hatchability). The inflection point occurs at a dietary selenium concentration of 3.9 mg/kg. (The Discussion section below describes uncertainty around the inflection point.) The predicted EC₁₀ is 4.4 mg/kg (just slightly above the inflection point) and the 95% CI around the predicted EC₁₀ ranges from 3.8 to 4.8 mg/kg. The predicted EC₁₀ of 4.4 mg/kg is slightly lower than Ohlendorf's (2003) EC₁₀ of 4.9 mg/kg, and the 95% CI is narrower using hockey stick regression than when using logistic regression.

Selenium in Bird Eggs

Similar to the dietary values calculated by Ohlendorf (2003) for reproductive toxicity for mallards, the EC₁₀ in eggs was reported as 12.5 mg/kg, with 95% CIs of 6.4 to 16.5 mg/kg (Figure 3). The EC₁₀ of 12.5 mg/kg was estimated by fitting a logistic regression model to the results of the six laboratory studies with mallards.

As noted in Table 2, the EC₁₀ for duckling mortality, as reported in Adams et al. (2003), ranged from 12 to 16 mg/kg (see Adams comments in Attachment B). These EC₁₀ values are based on a synthesis of laboratory studies in which the final endpoint was duckling mortality (the same effects data used in the dietary EC₁₀ evaluation with hockey-stick regression above) and the range of EC₁₀ values reflects different statistical approaches for analyzing the data. An adaptation from Figure 3 in Adams et al. (2003) is provided below (Figure 4), with the 95% CI included. As shown, the inflection point occurs at an egg selenium concentration of 9.8 mg/kg, with a predicted EC₁₀ comparable to that derived by Ohlendorf (2003). (See Discussion for comments concerning uncertainty around the inflection point.) However, the 95% CI using hockey-stick regression is much narrower (9.7 to 13.6 mg/kg) than that derived by Ohlendorf using logistic regression (6.4 to 16.5 mg/kg). Given that there is a clear egg-selenium threshold at which effects begin to be observed, a unimodal model, such as logistic regression, may result in exaggerated confidence intervals, particularly in the tails.

Discussion

Additional discussion is presented below concerning the basis for selection of threshold values, uncertainty surrounding the hockey-stick regression inflection points, hormetic effects of selenium, and other qualifications and points discussed during the Panel meeting in November, as reflected in comments from Panel members (Attachment B).

Basis for Selection of Threshold Values

The Science Panel can choose a scientifically-based threshold value or acceptable "benchmark" concentration based on the consensus confidence limits described by analysis of available data (presented above), but ultimately, a choice of numbers from within the consensus confidence limits for regulatory purposes is not a scientific decision. Choices of a specific number or numbers from within those confidence ranges are philosophical/legal decisions that depend on how precautionary the State of Utah wants to be (a matter of philosophy) and on how much potential for legal liability the State is comfortable with exposing itself to. The key decision the State must make is whether they want to regulate to a "NEC" (no effects concentration, which is not the same as a NOEC [no observed effects

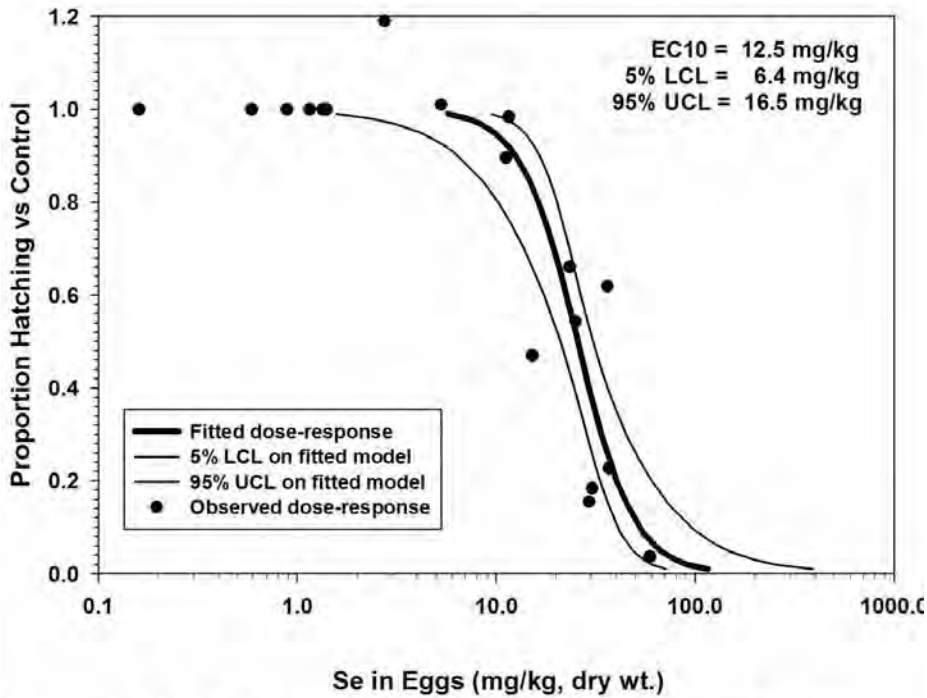


Figure 3. Mallard egg hatchability vs control as a function of selenium concentration in eggs.

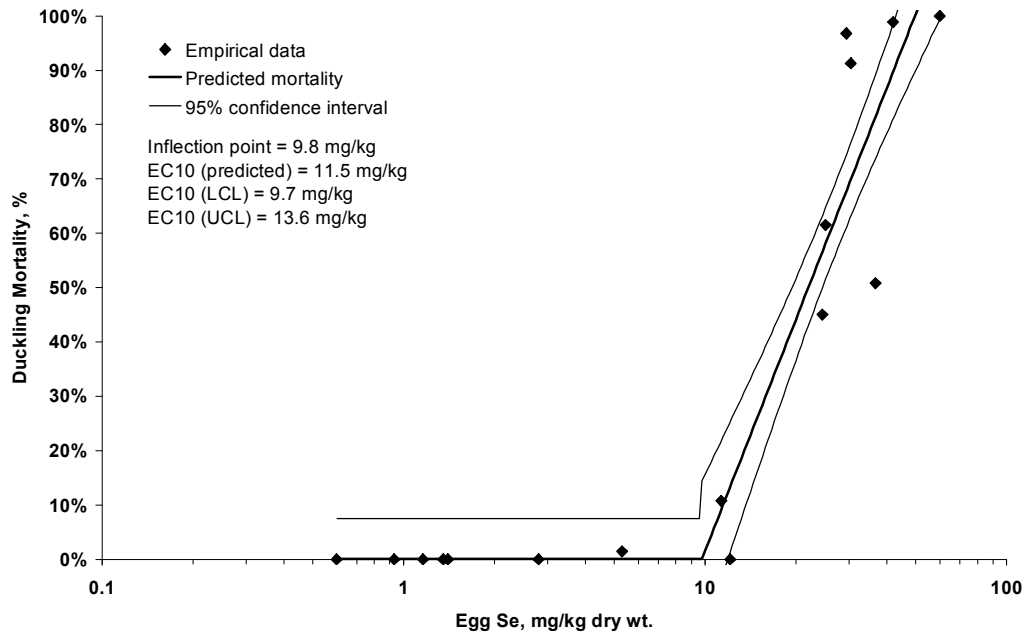


Figure 4. Hockey stick regression of laboratory mallard duckling mortality versus egg selenium.

concentration]) standard or to some version of a “tolerably toxic” standard such as an EC₁₀, an EC₂₀, or an EC₀₅, etc.

Conceptually, a benchmark concentration is defined as the location on the exposure-response curve that is the threshold between absence and presence of a given effect or endpoint (i.e., the threshold between an EC₀₀ and an EC₀₁ concentration [see: www.epa.gov/ecotox/ecoss1/pdf/ecoss1_attachment_3-2.pdf; p. A-6]). Benchmark concentrations are estimated as the lower 95 percent confidence boundary on the EC₁₀ (see: Meister and Van Den Brink [2000], pp. 114-116 in particular; and USEPA [2000]).

Uncertainty Surrounding the Hockey-Stick Regression Inflection Points

To determine the inflection point between the hockey-stick “blade” and “handle”, or any parameter in the model, initial parameter values are input to the software program SPlus® and an iterative technique is used to search for more exact parameter values that will minimize the sum of squared deviations between the observed effects data and effects values predicted by the model. Variance in the estimate of the inflection point value is affected by the spacing of the measured X values as well as the scatter or trend in Y values in the vicinity of the estimated inflection point. If, for example, there are few measured dietary selenium concentrations near the predicted inflection point, the uncertainty in the location of the inflection point will be greater because it will be difficult to determine the exact concentration at which the inflection point occurs (i.e., it could be between two of the measured values). Uncertainty around the predicted Y (EC) values at the predicted inflection point is affected by the number of Y values and the scatter of the Y values at that particular X value (which, when calculating the confidence interval around Y, is assumed to be estimated without error). Thus, both the spacing of the measured X values and the variance in the response variable affects the uncertainty around the inflection point. The tighter spacing and less ambiguous effects response after the inflection point causes the 95% CI around the dietary selenium-based inflection point (3.0 to 4.9 mg/kg) to be narrower than that for the egg selenium-based inflection point (6.4 to 14.9 mg/kg).

However, although there is uncertainty surrounding the inflection point, use of the best estimate of the inflection point results in the best fit of the regression model to the data. In Figure 4, for example, if the inflection point occurred at either end of the 95% CI of egg selenium concentration (6.4 to 14.9 mg/kg dry wt.) one can easily visualize that the fit of the regression to the data points above the inflection point would not pass through the measured values in the same way.

Hormetic Effects of Selenium

Consideration of the hormetic effects of selenium may result in lowering of thresholds (for hormetic substances and endpoints one has to distinguish between valid control responses and hormetic deficiency responses before a valid baseline to compare toxic responses against can be identified). The hormetic bias in the data used for the Ohlendorf (2003) regressions has not yet been fully considered by the Science Panel. If such consideration were to result in changes, those changes could only be in the direction of a downward shifting of the threshold confidence limits. (For example, preliminary unpublished analyses that adjusted for hormetic effects in the mallard data yielded a revised EC₁₀ for diet of

4.1 mg/kg, with a 95% CI of 1.3 to 5.8 mg/kg, and a revised EC₁₀ for eggs of 9.22 mg/kg, with a 95% CI of 4.11 to 13.07 mg/kg.).

Other Qualifications and Points Discussed

The Panel also discussed the following additional qualifications and points relative to toxicity threshold values:

- Applicability of laboratory data to field situations is not certain (note that field data were retained in compilation of egg-selenium concentrations in Table 2), and it is important to collect site-specific field data on selenium concentrations in bird eggs (e.g., current data gathering effort at the Great Salt Lake).
- Applicability of mallard data to species at Great Salt Lake is uncertain, because relative sensitivity of all species nesting there is not known.
- Threshold values discussed are for the hatchability endpoint (based on diet and avian egg) but non-reproductive adverse effects endpoints (e.g., avian blood endpoint) also may be important. However, interpretive values for selenium in avian blood are not available; although selenium concentrations in blood indicate exposure of the birds, that endpoint is not considered useful for setting a water quality standard.
- Phalaropes are seasonally numerous at the Great Salt Lake and should be added to the list of species to be monitored because they represent species with a feeding rate that is a large percentage of body weight (affecting energy consideration in determining wildlife criterion).

Recommended Next Steps

The issues summarized in this technical memorandum should be discussed/considered further by the Panel, particularly to refine the selection of threshold values for bird diets and eggs with respect to effects documented elsewhere (in field and laboratory studies) and considering the results being developed through research at the Great Salt Lake. In parallel, it will be important to know what level of protectiveness the State and EPA will apply in the development of the site-specific standard for selenium on the Great Salt Lake (i.e., EC₂₀, EC₁₀, EC₀₅, etc.) so that the Science Panel can most effectively make recommendations that can be applied toward that purpose.

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ATTACHMENT A
Tables

TABLE 1
Diet Concentrations

mg/kg	Approach or Site	Effects	Species	Reference(s)
4.87 (CI 3.56 - 5.74)	Synthesis of lab Data	Hatchability in mallards (10% effect level/95% confidence boundaries)	Mallard	Ohlendorf 2003
4.4 (CI 3.8 - 4.8)	Synthesis of lab data	EC ₁₀ for duckling mortality	Mallard	Bill Adams analyses presented in Attachment B
3.85 - 7.7 (diet based on 10% moisture)	Lab	Reduced hatching success in mallards (33% at 7.7 µg/g); reduced growth and weight in hatchlings	Mallard	Stanley et al. 1996
7.7 (diet based on 10% moisture)	Lab	Reduction in number of surviving mallard ducklings produced per female	Mallard	Stanley et al. 1996
8.8 4.4/6.2 (diet based on 10% moisture)	Lab	8.8 - LOAEL, 4.4 - NOAEL, 6.2 - Geometric Mean Reduction (17%) in survival of mallard ducklings; mean decrease (43%) in number of 6-day-old ducklings	Mallard	Heinz et al. 1989
6	Lab	Adverse effect on body condition of male American kestrels	American Kestrels	Yamamoto and Santolo, 2000
7.7 - 8.8 (diet based on 10% moisture)	Lab	Dietary threshold of teratogenic effects in mallards; above upper threshold, rate of deformity rises sharply	Mallard	Stanley et al. 1996
7.7 - 8.8 (diet based on 10% moisture)	Lab	Dietary threshold of mallard duckling mortality (parental exposure)	Mallard	Stanley et al. 1996

Note: Highlighted cells are the threshold values for bird diets identified by consensus of the Science Panel on November 30, 2006.

TABLE 2
Egg Concentrations

mg/kg (dry wt.)	Approach or Site	Effects	Species	Reference(s)
12.5 (CI 6.4 - 16.5)	Synthesis of lab data	Hatchability in mallards (10% effect level/95% confidence boundaries)	Mallard	Ohlendorf 2003
10	Synthesis of lab data	NOAEL	Mallard	Adams et al. 2003
12 - 16	Synthesis of lab data	EC ₁₀ for duckling mortality	Mallard	Adams et al. 2003
9	Synthesis of lab data	Impaired clutch viability (8.2% effects level)	Mallard	Lam et al. 2005
8.2 (or 7.3) (egg based on 73% moisture)	Field	16% depression in egg viability (7.3 in paper)	Spotted Sandpiper	Harding et al. 2005
6	Synthesis of field data	Threshold (3% effect level) of hatchability	Stilts	Skorupa, 1998; Skorupa, 1999
5.1 (egg based on 78.4% moisture)	Field	15% depression in egg viability	American dipper	Harding et al. 2005

Note: Highlighted cells are the threshold values for bird eggs identified by consensus of the Science Panel on November 30, 2006.

ATTACHMENT B

**Comments on December 8, 2006,
Draft Technical Memorandum**

Comments on December 8, 2006, Draft Technical Memorandum

Comments of Bill Adams

Following are comments on Harry Ohlendorf's draft technical memorandum to the Great Salt Lake Science Panel entitled *Threshold Values for Selenium in Great Salt Lake: Selections by the Science Panel* (December 8, 2006).

Selenium in Bird Diets

As noted in the draft memorandum, the mallard studies used in Ohlendorf (2003) as the basis for a dietary selenium EC10 in birds was based on a "dry diet" containing about 10% moisture. Although the moisture content of the mallard diet was low, we recommend that standard convention should be used to properly adjust the dietary selenium concentrations to a dry weight basis. The equation for the wet weight-to-dry weight conversion is included in Attachment 1 to this memorandum.

In Adams et al. (2003), hockey-stick regression was used to model relationships between egg selenium concentrations and adverse effects in order to derive toxicity thresholds, such as EC10 values. Hockey-stick regression is a model that has been used to define a threshold when an underlying background level of response is unrelated to the dose. Thus, such a model may be relevant to naturally occurring elements that are essential to birds and a wide variety of other organisms and particularly useful for elements such as selenium, which has a narrow range between levels that are essential and levels that are toxic to birds so that variance around the inflection point (threshold) in the model is small. As shown in Figure 1 below, a threshold clearly appears to exist when dietary selenium is plotted versus duckling mortality (which incorporated the cumulative effects of fertilization success and hatchability). The inflection point occurs at a dietary selenium concentration of 3.9 mg/kg dry wt. (please see discussion at end of comments concerning uncertainty around the inflection point). The predicted EC10 is 4.4 mg/kg dry wt. (just slightly above the inflection point) and the 95% confidence interval around the predicted EC10 ranges from 3.8 to 4.8 mg/kg dry wt. The predicted EC10 of 4.4 mg/kg dry wt. is slightly lower than Harry Ohlendorf's EC10 of 4.9 mg/kg dry wt., but the 95% confidence interval is narrower using hockey stick regression.

Selenium in Bird Eggs

As noted in Table 2 of the draft memorandum, the EC10 for duckling mortality, as reported in Adams et al. (2003), ranged from 12-16 mg/kg dry wt. These EC10 values are based on a synthesis of laboratory studies in which the final endpoint was duckling mortality (the same effects data used in the dietary EC10 evaluation above) and the range of EC10 values reflects different statistical approaches for analyzing the data. An adaptation from Figure 3 in Adams et al. (2003) is provided below, with the 95% confidence interval included. As

shown, the inflection point occurs at an egg selenium concentration of 9.8 mg/kg with a predicted EC10 comparable to that derived by Harry Ohlendorf (please see discussion at end of comments concerning uncertainty around the inflection point). However, the 95% confidence interval using hockey stick regression is much narrower (9.7 to 13.6 mg/kg dry wt.) than that derived by Harry using logistic regression (6.4-16.5 mg/kg dry wt.). Given that there is a clear egg selenium threshold at which effects begin to be observed, a unimodal model, such as logistic regression, may result in exaggerated confidence intervals, particularly in the tails.

Uncertainty Surrounding the Hockey-Stick Regression Inflection Points

To determine the inflection point between the hockey-stick “blade” and “handle”, or any parameter in the model, initial parameter values are input to the software program SPlus® and an iterative technique is used to search for more exact parameter values that will minimize the sum of squared deviations between the observed effects data and effects values predicted by the model. Variance in the estimate of the inflection point value is affected by the spacing of the measured X values as well as the scatter or trend in Y values in the vicinity of the estimated inflection point. If, for example, there are few measured dietary selenium concentrations near the predicted inflection point, the uncertainty in the location of the inflection point will be greater because it will be difficult to determine the exact concentration at which the inflection point occurs (i.e., it could be between two of the measured values). Uncertainty around the predicted Y (EC) values at the predicted inflection point is affected by the number of Y values and the scatter of the Y values at that particular X value (which, when calculating the confidence interval around Y, is assumed to be estimated without error). Thus, both the spacing of the measured X values and the variance in the response variable affects the uncertainty around the inflection point. The tighter spacing and less ambiguous effects response after the inflection point causes the 95% confidence interval around the dietary selenium-based inflection point (3.0 to 4.9 mg/kg dry wt.) to be narrower than that for the egg selenium-based inflection point (6.4 to 14.9 mg/kg dry wt.).

However, although there is uncertainty surrounding the inflection point, use of the best estimate of the inflection point results in the best fit of the regression model to the data. In Figure 2, for example, if the inflection point occurred at the either end of the 95% confidence interval of egg selenium concentration (6.4 to 14.9 mg/kg dry wt.) once can easily visualize that the fit of the regression to the data points above the inflection point would not pass through the measured values in the same way.

Figure 1. Hockey stick regression of laboratory mallard duckling mortality versus dietary selenium.

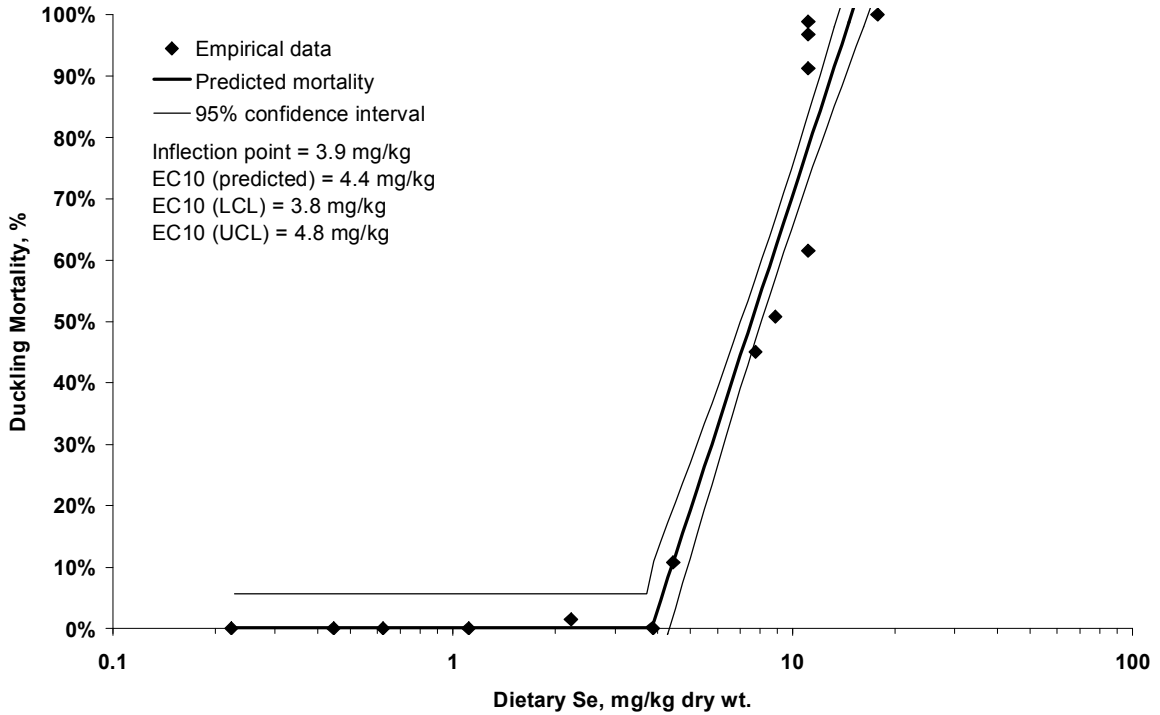
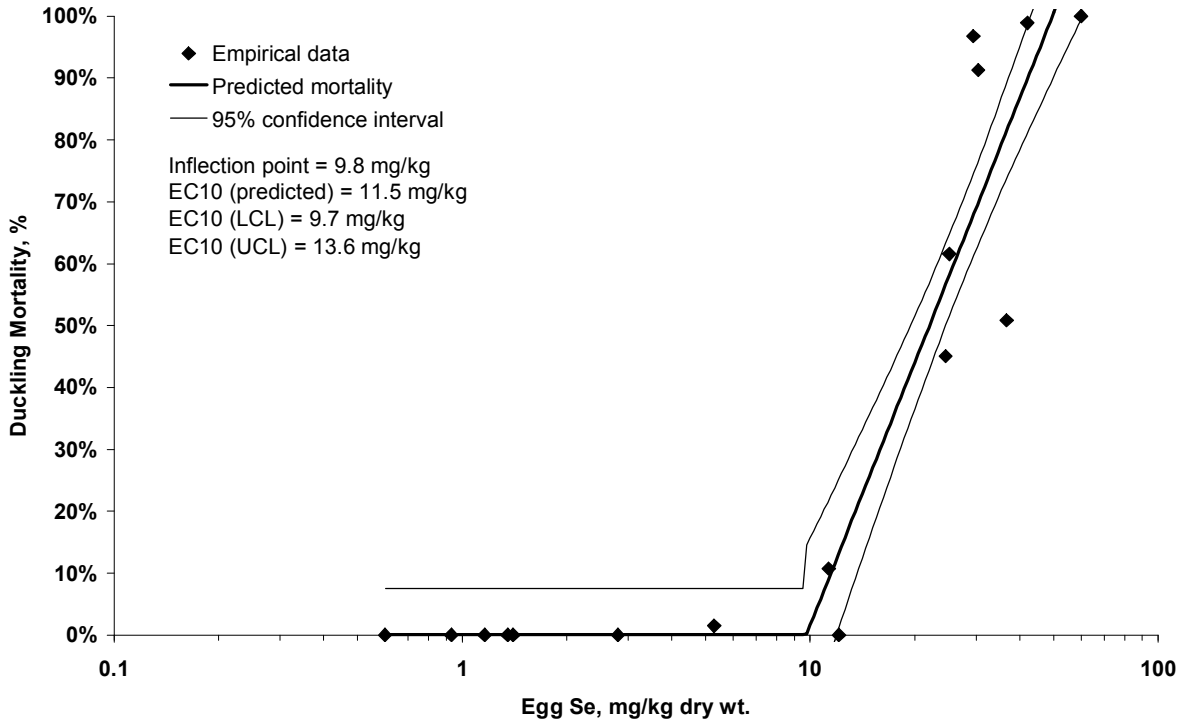


Figure 2. Hockey stick regression of laboratory mallard duckling mortality versus egg selenium.



ATTACHMENT 1

WET WEIGHT-TO DRY WEIGHT CONVERSION FOR DIETARY SELENIUM CONCENTRATIONS IN MALLARD STUDIES

$$\text{Dry Weight Concentration} = \frac{\text{Wet Weight Concentration}}{f_{\text{solids}}}$$

Where: f_{solids} = fraction solids in diet (i.e., 0.9 in a diet containing 10% moisture)

Comments of Anne Fairbrother

I realize that I am late (the last?) on providing comments and feedback on the report you pulled together from our last Salt Lake City meeting on threshold values. I was sort of hoping to see the data from Bill Adams' re-analysis of the dose-response before replying... Absent that, here are my thoughts and comments.

I think you did an appropriate job pulling together what was discussed at the meeting in regard to diet and egg threshold levels. However, the more I look at the data in regard to selenium uptake and effects, the more convinced do I become that we are dealing with a threshold phenomenon, likely because of the essential nature of the element. I do believe that the mean value for the EC10 that was selected for both endpoints is likely to remain pretty much the same regardless of what dose-response model is used, but the standard error about the mean may be different. Likely it will be smaller when using a threshold model since a logistic model tends to spread out the CI's at its tails. So, for now, I am willing to approve the document as a report of what was discussed at the meeting, but not as a final say on what we have agreed to for the EC10 and its confidence intervals.

Comments of Theresa Presser

Suggested additions to threshold discussion write-up of 12/8/06:

- 1) Page 1: Note that compilation of data for consideration was adapted from Presser and Luoma (2006), table 15.
- 2) Page 1: Note that in addition to laboratory data, a compilation of field data for egg concentrations was retained.
- 3) Page 1: Note that any final determination must take into account site-specific data currently being generated by the Great Salt Lake research effort.
- 4) Page 2 wording: "The panel agreed by consensus that the 95% CIs on mean selenium concentrations in mallard diet and eggs would be reasonably protective for birds nesting at the Great Salt Lake, and the range of values included the concentrations proposed by various panel members for consideration. Rational supporting selection of the 95% CIs is provided by the previous technical memorandum and through discussion at the panel meeting."
 - a) Did you mean here the 95% CIs on the mean EC10 for hatchability?
 - b) The phrase "would be reasonably protective for birds nesting at the Great Salt Lake" does not adequately convey all parts of the extensive discussion that took place. I did not perceive that a consensus had been reached as to protectiveness, only that a consensus had been reached as to the interpretation of data from mallard lab experiments. Therefore, I suggest incorporating into the wording of a summary statement the following qualifications and points that were discussed at the meeting:
 - 1) Applicability of lab data to field situations (note retention of compilation of field data in table 2 and current data gathering effort at the Great Salt Lake; points 2 and 3 listed above)
 - 2) Applicability of mallard data to species at Great Salt Lake (sensitivity issue)
 - 3) Applicability of hatchability endpoint (diet and avian egg) and non-reproductive adverse effects endpoints (e.g., avian blood endpoint)
 - 4) Level of protection and precautionary regulation as exemplified by benchmark concentration regulation. Specifically add excerpt from page 8 of 11/28/06 memo as clarification of 95% CI: "Conceptually, a benchmark concentration is defined as the location on the exposure-response curve that is the threshold between absence and presence of a given effect or endpoint, i.e., the threshold between an EC00 and an EC01 concentration (see: www.epa.gov/ecotox/ecossl/pdf/ecossl_attachment_3-2.pdf; p. A-6)..... Benchmark concentrations are estimated as the lower 95% confidence boundary on the EC10 (see: Meister, R., and P.J. Van Den Brink. 2000. The analysis of laboratory toxicity experiments. Pages 99-118 in T. Sparks (ed.), Statistics in Ecotoxicology. John Wiley & Sons, LTD, New York, NY: [pp 114-116 in particular]; and see: USEPA. 2000. Benchmark Dose Technical Guidance

Document. [External Review Draft]. EPA/630/R-00/001. U.S. Environmental Protection Agency, Washington, DC.”

- 5) Addition of phalarope to list of species to be monitored to represent species with a feeding rate that is a large percentage of body weight (energy consideration in determining wildlife criterion).
 - 6) Potential lowering of thresholds through consideration of hormesis data (for hormetic substances and endpoints one has to distinguish between valid control responses and hormetic deficiency responses before a valid baseline to compare toxic responses against can be identified).
- 5) References: Add Presser and Luoma, 2006.
- 6) Table 1: “Bill Adams suggestion” needs to be documented as how his entry differs from entry #1 in table 1.

Comments of Joe Skorupa

In Table 1 I don't believe the science panel wanted the value of 4.87 to be presented in bold type, only the confidence limits (for comparison see Table 2 where I think you have it the way the science panel intended).

Adjusting for 10% moisture would result in an 11% increase in the dietary values, not an upward adjustment of 10% as stated.

I didn't feel like your draft write-up adequately conveyed our (sci. panel's) discussion concerning the fact that, ultimately, a choice of numbers from within the consensus confidence limits is not a scientific decision. That confidence range is as far as science can bring us... choosing a specific number or numbers from within those confidence ranges are philosophical/legal decisions that depend on how precautionary the State of Utah wants to be (a matter of philosophy) and on how much potential for legal liability the State is comfortable with exposing itself to. The key decision the State must make is whether they want to regulate to a "NEC" (no effects concentration... which is not the same as a NOEC) standard or to some version of a "tolerably toxic" standard such as an EC-10, or EC-20, or EC-05 etc.

Finally, I think on the scientific side of things we would be remiss in our duty as experts not to include some discussion indicating that the issue of hormetic bias in the data used for the Ohlendorf (2003) regressions has not yet been fully considered by the science panel (at Bill Adams request to defer it so that he could preview Beckon's SETAC presentation before I presented any of it to the panel... although it seemed to be acceptable to everyone to see Kennecott's U. of Wyoming presentation without any opportunity for anyone other than Bill A. to preview it... seems like a double standard to me), and that if such consideration were to result in changes, those changes could only be in the direction of a downward shifting of the threshold confidence limits.

For example, remember that the analysis that Brad Sample re-ran to adjust for hormetic effects in the mallard data yielded a revised EC-10 for diet of 3.7 ppm ww [4.1 ppm dw] with a 95% confidence interval of 1.15 - 5.18 ppm ww [1.3 - 5.8 ppm dw] and a revised EC-10 for eggs of 9.22 ppm dw with a 95% confidence interval of 4.11 - 13.07 ppm dw.

APPENDIX C

ALLOMETRIC ADJUSTMENT OF DIETARY CONCENTRATIONS

The Appendix explains the approach used to allometrically adjust dietary toxicity threshold for birds. In ecological risk assessments for birds, dose-based toxicity reference values (TRVs) are used to estimate toxic effects. Toxicity reference values are calculated using the following equation:

$$TRV_t = \frac{EPC \times IR \times FC \times AF}{BW}$$

where:

- TRV_t = Toxicity reference value for the test species.
- EPC = Exposure point concentration; i.e., the dietary concentration of a chemical that produced the toxic effects measured in the toxicity study (mg/kg-dw).
- IR = Food ingestion rate (mg/day-dw).
- FC = Fraction contacted (unitless; assumed to be 1).
- AF = Assimilation fraction (unitless; assumed to be 1).
- BW = Body weight (kg).

Toxicity reference values are allometrically adjusted using the following equation (Sample and Arenal 1999):

$$TRV_a = TRV_t \times \left(\frac{BW_t}{BW_a} \right)^{(1-b)}$$

where:

- TRV_a = Allometrically adjusted toxicity reference value.
- TRV_t = Toxicity reference value for the test species.
- BW_t = Body weight of the test species.
- BW_a = Body weight of species for which the allometric adjustment is being performed.
- b = Allometric scaling factor (unitless).

The $\left(\frac{BW_t}{BW_a}\right)^{(1-b)}$ term in the equation above is also referred to as an “allometric adjustment factor”. Combining the above two equations, and eliminating the variables assumed to equal 1, produces the following equation:

$$\frac{EPC_a \times IR_a}{BW_a} = \left[\frac{EPC_t \times IR_t}{BW_t} \right] \times \left(\frac{BW_t}{BW_a} \right)^{(1-b)}$$

By re-arranging the equation above, it is possible to derive an allometrically adjusted dietary concentration protective of specific toxic effect. The re-arranged equation is as follows:

$$EPC_a = \left[\frac{BW_a}{IR_a} \right] \times \left[\frac{EPC_t \times IR_t}{BW_t} \right] \times \left(\frac{BW_t}{BW_a} \right)^{(1-b)}$$

Allometrically adjusted dietary thresholds were calculated for the avian species of concern in the Bay identified by USFWS (2007):

- Bald eagle
- California clapper rail
- Greater scaup
- Lesser scaup
- White-winged scoter
- Surf scoter
- Black scoter

The test species from which the TRVs were allometrically adjusted include:

- Leghorn chicken
- Mallard
- Screech owl

The body weights for all of these birds are provided in Table C-1 below. Ingestion rates for each bird species were calculated from their body weights using the equations provided by Nagy (2001). The ingestion rate equations and calculated ingestion rates are also shown in Table C-1 below.

Table C-1
Body weights and ingestion rates.

Bird species	Body Weight (g)	Ingestion Rate Equation ^f		Ingestion Rate (mg/day-dw)
Bald eagle ^a	5,275	Carnivorous birds	$y = 0.849*(x)^{0.663}$	249,311
California clapper rail ^a	346	Marine birds	$y = 0.880*(x)^{0.658}$	41,228
Greater scaup ^a	959	Marine birds	$y = 0.880*(x)^{0.658}$	80,634
Lesser scaup ^a	663	Marine birds	$y = 0.880*(x)^{0.658}$	63,247
White-winged scoter ^a	1,917	Marine birds	$y = 0.880*(x)^{0.658}$	127,189
Surf scoter ^b	1,047	Marine birds	$y = 0.880*(x)^{0.658}$	85,429
Black scoter ^a	987	Marine birds	$y = 0.880*(x)^{0.658}$	82,198
Mallard ^c	1,214	Marine birds	$y = 0.880*(x)^{0.658}$	94,167
Chicken ^d	1,800	Galliformes	$y = 0.088*(x)^{0.891}$	69,973
Screech Owl ^e	186	Carnivorous birds	$y = 0.849*(x)^{0.663}$	27,139

Notes:

a - female body weight from USFWS (2007)

b - female body weight from BNA (2007)

c - body weight is from Heinz et al. (1989) and is average of females at time of sacrifice in all treatments except 16 mg/kg

d - egg laying leghorn chickens average 1,800 g (National Research Council 1994)

e - body weight is from Wiemeyer and Hoffman (1996) and is average of females at time of sacrifice in all treatments

f - from Nagy (2001)

The body weights and ingestion rates from Table C-1 were used to calculate allometric adjustment factors and allometrically adjusted dietary threshold concentrations for the species of concern in the Bay (Table C-2).

Table C-2
Allometric adjust factors and allometrically adjusted dietary thresholds.

Bird species	Allometric Adjustment Factor (-) for Dietary Screening Values from			Dietary Screening Value (mg/kg-dw) Adjusted from		
	Mallard ^a	Chicken	Screech Owl	Mallard ^a	Chicken ^b	Screech Owl ^c
Bald eagle	1.34	1.24	1.95	9.7	4.0	104.3
California clapper rail	0.78	0.72	-	2.2	0.9	-
Greater scaup	0.95	0.88	-	3.9	1.6	-
Lesser scaup	0.89	0.82	-	3.2	1.3	-
White-winged scoter	1.10	1.01	-	5.6	2.3	-
Surf scoter	0.97	0.90	-	4.1	1.7	-
Black scoter	0.96	0.89	-	3.9	1.6	-

Notes:

a - EC10 for reduced hatching success from Adams et al. (2003) Ohlendorf (2007) of 4.4 mg/kg-dw

b - effect threshold for reduced hatching success of 3.9 mg/kg-dw from Ort and Latshaw (1978)

c - effect threshold for reduced hatching success of 17.3 mg/kg-dw from Wiemeyer and Hoffman (1996)

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1 Introduction

The Regional Water Board's 2010 Amendment of Waste Discharge Requirements for San Francisco Bay Region Refineries, Order R2-2010-0057 (Order), was adopted in March 2010. It directed the refineries to implement effluent and receiving water selenium characterization studies as set forth in Table 4 of the Order.

Table 4 prescribed a deadline of May 1, 2010 to submit this Study Plan (Plan) which was amended to June 7, 2010, by the Board staff in their April 15, 2010 letter to the Western States Petroleum Association (WSPA). A meeting was held with the Water Board on July 8, 2010 to discuss comments and recommended changes to the Study Plan. Technical discussions on the number and location of samples continued until 24 August 2010. This version of the Study Plan incorporates all changes that were discussed.

This Plan outlines the steps, events, and a schedule for accomplishing the tasks in Table 4 of the Order, and provides three key tasks (below) that are outlined in greater detail further in this section:

Task 1. Conduct Sampling and Analysis

Task 2. Preparation of Status Reports

Task 3. Preparation of Final Study Report

The work in this Plan will be performed by Tetra Tech staff in Lafayette, California with the support of Dr. Greg Cutter at Old Dominion University, and Pacific EcoRisk of Fairfield, California. The laboratory analysis of water samples will be performed in the laboratory of Greg Cutter at Old Dominion University, following protocols similar to those used in most previous selenium speciation analyses in the bay and referred to in the TMDL support documents (Tetra Tech, 2010). The field sampling will be conducted jointly by Tetra Tech and Pacific EcoRisk. Additional details on the study team are provided below.

This Plan contains seven elements ("a" through "g") directly corresponding to the elements under Task 1 of Table 4 in the Order. Each section describes how each of these elements in the Plan will be addressed.

Elements a, b, c

Table 1 below describes Plan elements a, b, and c. The numbers of samples to be collected for each sample type are described in Table 2. The samples at the five refineries are identified as Sample Types 1 and 2. During the first year, effluent samples will be collected monthly at each refinery. These effluent samples will be composite samples that are collected separately from the monthly compliance samples. These special samples will be collected at different times from the compliance samples and sent to the Old Dominion University research laboratory of Greg Cutter for the purposes of the speciation analyses. The results will be reported in the annual status

reports described in Task 2 below. The receiving water in the vicinity of the five refinery discharges will be sampled in the two major sampling events (wet and dry seasons) in year 1.

**Table 1
Sample Plan Description**

Element	Permit Language	Plan
a	Effluent and receiving water sampling locations (the effluent sampling location may be the existing effluent compliance sampling point; receiving water sampling locations shall be within a 100-foot radius of the outfall to characterize near-field concentrations and speciation);	Monthly effluent samples and receiving water transects at the 5 refineries during year -1 sampling.
b	Receiving water sampling along transects from the Pacific Ocean (Golden Gate) to the Sacramento River (Rio Vista) and San Joaquin River (USGS Station 757), including sampling in the freshwater portions of the rivers at Vernalis (San Joaquin River) and Freeport (Sacramento River);	Transect sampling in the estuary, stations in the Sacramento and San Joaquin Rivers (at Vernalis and Freeport), and a Pacific Ocean location outside Golden Gate
c	Sampling and analysis protocols (including means to evaluate seasonal conditions under low and high flows from the Sacramento / San Joaquin River Delta, selenium concentrations in the water column and suspended particles, and speciation and particulate selenium content in the effluent);	1 dry season sampling in 2010, 1 wet and 1 dry season sampling in 2011, and 1 wet season sampling in 2012

**Table 2
Number of Samples to be Collected and Analyzed**

	Element	Samples/ Event	Events	Years	Total Number of Samples
1	Refineries, effluent	5	12	1	60
2	Refineries, receiving water	15	4	1	60
3	Sacramento, San Joaquin Rivers (at Vernalis and Freeport)	2	2	2	8
4	Transect, Rio Vista to GGB	19	2	2	76
					204

Three receiving-water samples will be collected at each refinery. Figure 1 provides a conceptualization of two typical multipoint diffusers at the refineries. The effluent is discharged from multiple ports spaced over the diffuser section. The outfalls that lead to the diffusers are not shown. Buffer lines of 5 m, 10 m, and 20 m are shown for the smaller diffuser, and an additional buffer line of 50 m is shown for the larger diffuser. Example sampling stations are also shown in Figure 1, but as described below, the exact sampling locations will not be selected until after a planned reconnaissance survey.

Rationale for selection of sampling locations.

- **Locations are chosen to be near completion of initial mixing.** Initial dilution is typically attained within 5 m to 15 m of the diffusers, based on dye studies and dilution modeling that have been completed over the years at these locations. The zone of initial dilution (ZID) dynamically changes location and size over time, so sampling stations on the up-estuary and down-estuary sides of the diffuser are appropriate. The locations of the sampling stations in the schematic diagram (Figure 1) are shown directly over the centerline of the diffuser and 10 m off the diffuser for a total of three locations per diffuser. However, some of the discharges are located near wharf structures, and the exact locations of the sampling stations will be based on the results of a reconnaissance survey

conducted prior to the first sampling event. The reconnaissance survey will be conducted to determine the feasibility of collecting samples above centerline of the diffuser and at locations at the boundary of the calculated ZID. The safety of the boat-based sampling crew will also be a primary consideration in selecting the sampling locations.

- ***Sampling will be conducted near slack tide.*** Slack tide typically provides a more critical situation for the attainment of initial dilution (lower initial dilutions).
- ***Sampling will be performed in the fall near the end of the dry season.*** While water column stratification may be minimal at that time, current speeds will be low.
- ***Samples will be taken at prescribed depths.*** The wastewater plumes typically begin to rise in the water column as they are discharged due to buoyancy and momentum effects. However, the plume may not surface due to effects such as stratification. To account for this potential effect, and the fact that previous dye studies showed that wastewater plumes were at times trapped beneath the surface, the samples will be collected at locations no closer than 2 m to 3 m below the water surface, and several meters above the discharge depth.

Additional issues associated with accurately identifying sampling locations.

Locations of each diffuser are presently given by latitude/longitude information. However, this information is not sufficiently accurate to precisely locate the diffusers. Consequentially, once the conceptual locations are selected, that information will be distributed to the refineries for review. Ultimately, outfall centerline locations should be located by direct visual inspection or by another reliable method. This location will become one of the three locations sampled per outfall. The two other sampling locations will be located relative to the first location. This approach is intended to minimize the possibility of conducting sample collection at locations that are well outside the ZID.

The objective of the receiving-water sampling is to characterize the mixing characteristics of the discharge and the speciation of the selenium upon initial dilution in the receiving water. All refinery samples will be analyzed for the dissolved and particulate selenium species described in Sampling Plan Element e below.

In each of the 4 major sampling events, samples will be collected on the Sacramento River at Freeport and on the San Joaquin River at Vernalis. These samples will establish new endpoint locations that will be used to establish the boundary conditions for the modeling and analysis efforts described below in Sampling Plan Element f. The transect sampling is the largest sample type. Samples will be collected along transects from the Pacific Ocean to the Sacramento River at Rio Vista and the San Joaquin River at USGS Station 757. This sampling and analysis effort will be conducted in both the wet and dry seasons over a 2-year period. The sampling stations along the transect will be spaced at 1.5 PSS salinity intervals. The results will be directly comparable to the results of the sampling previously conducted over the period 1997–2000 (Cutter and Cutter, 2004).

Element d

Table 4 in the Order requires a “comparison of the proposed protocols and analytical methods to previous sampling efforts.” As above, the previous efforts are understood to be the published papers of Greg Cutter’s research group at Old Dominion University (Cutter and San Diego-McGlone, 1990; Cutter and Cutter, 2004; Doblin et al., 2006). No other research group in the

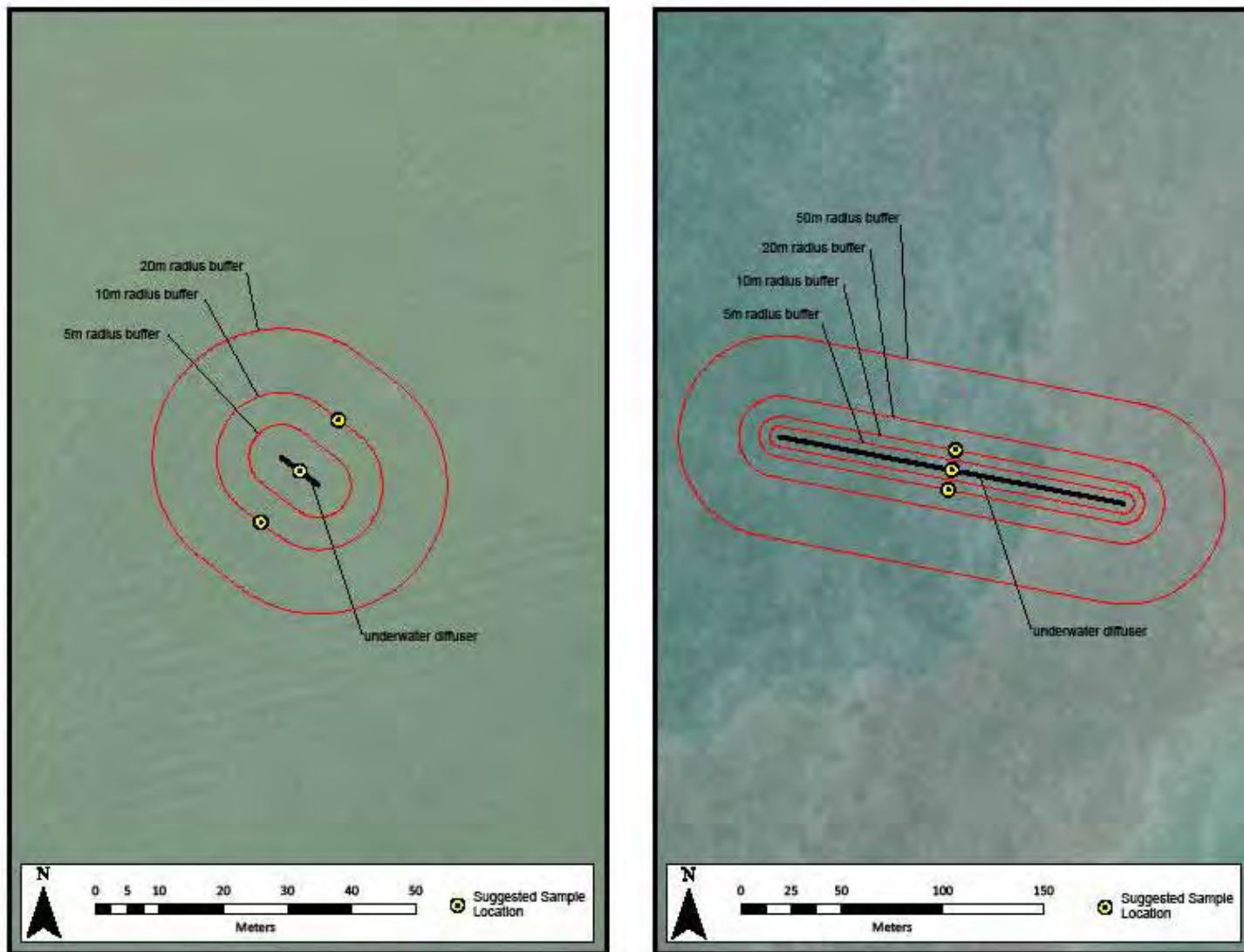


Figure 1. Schematic of proposed receiving-water sampling locations.

United States has collected this type of selenium species data in the San Francisco Bay.¹ To address Element d, Professor Cutter's group will conduct the laboratory analyses to replicate as closely as possible the analytical methods that were used in prior work. The analytical methods proposed to be used are summarized in Box 1, Sample Analyses (below) will provide the most direct and credible comparison of selenium species concentrations across a nearly 3-decade period (1986–2012).

Element e

This element outlines the chemical parameters that will be measured. The following analyses to be performed are:

- Salinity, total organic carbon, total nitrogen, nitrate plus nitrite, phosphate, silicate, chlorophyll-a (receiving water stations only), and total suspended material (TSM). Nitrate plus nitrite, phosphate, and silicate are not explicitly called for in the permit requirements, but are useful representations of bioavailable nutrients for algal growth and determined through a colorimetric process (see Box 1).
- Dissolved selenium: selenate (Se+6), selenite (Se+4), organic selenides (Se-2) (receiving water stations, boundary stations and effluent samples).
- Particulate selenium: selenate + selenite (adsorbed), organic selenide, and elemental selenium (receiving water stations, boundary stations, and effluent samples).

The measured total and dissolved selenium concentrations will be comparable to the total and dissolved selenium concentrations reported by the Regional Monitoring Program. Particulate selenium concentrations will be reported in both $\mu\text{g/L}$ and $\mu\text{g/g}$ units.

As noted above, the selenium species measurements will use the methods outlined in Box 1 (below). The analytical methods are designed to accurately and precisely determine dissolved and particulate selenium speciation at the very low concentrations found in San Francisco Bay.

Element f

This element will address the data interpretation models and other methods to be used. This will be done through the use of the ECoS-based selenium fate and transport model that was completed as part of TM-6 developed in support for the selenium TMDL. The new data to be collected will be used to test model performance and to run new model scenarios in order to enhance the credibility of the model; these efforts will provide additional support for its use in TMDL scenario planning. The model represents processes at a daily level and allows consideration of a variety of hydrologic and seasonal conditions (e.g., wet and dry seasons; wet, dry, and critically dry years).

Element g

This element outlines the implementation schedule. The initial sampling event is scheduled to begin on September 8, 2010. Subsequent sampling is planned for the 2-month windows shown below.

- Beginning 8 September 2010
- February–March 2011
- August–September 2011
- February–March 2012

¹ For example, the Regional Monitoring Program does not report selenium species data in the bay. Also, the USGS performs analysis on selenium in bivalves, but does not report water column selenium species.

Box 1. Sample Analyses

- I.** The speciation of dissolved selenium will be determined using the selective hydride generation/atomic absorption detection method described by Cutter (1978; 1982; 1983). Briefly, within a glass stripping vessel selenite is quantitatively converted to hydrogen selenide using sodium borohydride addition to a sample containing sulfanilamide to eliminate interference due to nitrite and acidified to 4 mol l⁻¹ HCl. The evolved hydrogen selenide is stripped from solution using helium and trapped in a borosilicate U-tube packed with silanized glass wool and immersed in liquid nitrogen. After the trap is removed from the LN₂, an atomic absorption spectrometer fitted with a open quartz tube furnace burning an air-hydrogen flame is used to detect the hydride; instrument response (as peak area) is recorded on a chromatographic integrator. To determine selenate+selenite, another acidified sample is boiled for 15 minutes, cooled, and then subjected to the selenite determination; selenate is the difference between this determination and that of selenite. Total dissolved selenium is determined by boiling a 4 mol l⁻¹ HCl acidified sample, with the addition of potassium persulfate, and then following the selenite procedure. The difference between total dissolved selenium and selenite+selenate yields the concentration of dissolved organic selenide + elemental selenium (this may be colloidal and pass through the 0.45 µm filter). However, many studies have shown that this fraction is primarily organic selenide in the form of dissolved peptides (Cutter, 1982; Cutter and Bruland, 1984; Cutter and Cutter, 1995), and hereafter it is referred to as “dissolved organic selenide.” To ensure accuracy, all determinations will utilize the standard additions method of calibration, and all samples will be analyzed in triplicate to quantify precision (found to be < 4% for concentrations above 0.03 µg/l). Detection limits for all three selenium forms are 0.0016 µg/l.
- II.** The total selenium content of suspended particles and phytoplankton cultures will be determined using wet oxidative digestion followed by selective hydride generation atomic absorption spectroscopy (Cutter, 1978, 1983). Filters are dried at 40° C, weighed (for TSM concentration), and subsequently digested using a three step nitric-perchloric acid reflux procedure (Cutter, 1985), but using an automated microwave digestion system with microwave-assisted evaporation. After evaporation of most of the nitric acid, the residue is redissolved in 4M HCl, passed through a column filled with Bio-Rad AG1 x 8 anion exchange resin (chloride form, 100-200 mesh) to remove iron and stored until final selenium analyses. Selective leaches will be conducted for determination of particulate selenium speciation (elemental selenium, Velinsky and Cutter 1990; SeIV + SeVI selenium, Cutter 1985). Aliquots of the digestion or selective leach solutions will be analyzed using the total dissolved selenium procedures of Cutter (1982, 1983). The standard additions method of calibration is used to ensure accuracy, and all determinations are made in triplicate. Accuracy will also be determined using the digestion and analysis of standard reference material (NIST 1566 or 1566b Oyster Tissue), for which recoveries will have to be within 1 standard deviation of the certified values to be accepted. The detection limit for particulate selenium is 0.0004 µg/l, with precision (as relative standard deviation) being better than 5%.
- III.** Filters for organic carbon and nitrogen analyses will be dried at 40° C and processed using a Elementar Micro-cube Elemental Analyzer (Cutter and Radford-Knoery, 1991). Chlorophyll-a will be extracted in 90% acetone in the dark at 4° C and determined using the fluorometric method of Strickland and Parsons (1972).
- IV.** The nutrients phosphate, silicate, and nitrate+nitrite will be determined using the colorimetric methods of Parsons et al. (1984), modified for use by an Astoria-Pacific rapid flow analyzer. Salinity is determined using a Portasal salinometer with IAPSO standard seawater as the reference.

Task 1. Conduct Sampling and Analysis

The field sampling will be performed beginning in September 2010, and will be repeated 3 more times to capture wet and dry conditions between 2010 and 2012 as noted above. Field sampling will include ocean, estuary, refinery effluent discharge, and river stations that are shown in Figure 2. Most stations will be at fixed locations, with the exception of estuary stations that capture the salinity gradient and are measured at similar salinity increments (typically, 2 salinity units). These stations may fall at different locations depending on the tidal stage. This protocol is consistent with that previously applied in the estuary. All ocean, estuary, and refinery effluent discharges will be accessed by a boat operated by Pacific EcoRisk, or by bridges over rivers where such access exists (Vernalis and Freepoint). The first sampling event will be conducted with Old Dominion University staff, who will also train Pacific EcoRisk and Tetra Tech staff in sample collection and on-boat sample processing techniques for trace-level selenium determination. Refinery effluent sampling will be conducted over the same period as the sampling in the estuary. Access to refineries will be arranged in consultation with the individual facilities.



Figure 2. Sampling locations indicating the bay locations (yellow symbols), the refineries (pink), the riverine boundaries (green), and the ocean boundary (blue).

Water samples will be acquired with 5 L Go-Flo bottles deployed on a Kevlar cable and triggered with a plastic messenger 1 m below the surface. After recovery, the bottle is pressurized with 8 psi nitrogen and water directed through a precleaned and tared 142 mm diameter, 0.45 μm polycarbonate membrane held in a Teflon filter holder for TSM and total particulate selenium determinations; an additional 250–500 ml will be filtered through 47 mm, 0.45 μm polycarbonate membranes for particulate selenium speciation. Membranes for particulate selenium analyses are carefully folded, placed in polyethylene vials, and immediately frozen. Filtered water is placed in 1 L borosilicate bottles (Teflon-lined caps), acidified to pH 1.6 with HCl, and stored in the dark.

until analysis for Se speciation. Filtered water is also placed in 125 mL borosilicate bottles for salinity/chlorinity determinations, and 125 mL polyethylene bottles that are immediately frozen for nutrients. In addition to particulate selenium samples, filtered samples will be collected for chlorophyll (pre-cleaned GF/F (Whatman) filters) and particulate organic carbon and nitrogen (13 mm GF/F filters); these will be frozen and stored using liquid nitrogen.

River inputs will be taken at Vernalis for the San Joaquin River and at Freeport on the Sacramento River using a trace metal clean pumping and filtration (0.45 µm) system. Samples will be treated and stored in the same manner as those for the estuarine transects. Refinery effluent samples will be collected as 24 hour composites into 2 L polyethylene bottles, vacuum filtered through a 0.45 µm membrane, and the filtrate acidified and treated like an estuarine or river sample.

All of these field methods are identical to those used by Greg Cutter's laboratory for SF Bay sampling in 1986 (Cutter, 1989; Cutter and San Diego-McGlone, 1990; Cutter and Cutter, 2004; Doblin et al., 2006), and have been optimized for taking representative and unaltered samples for the concentration and speciation of dissolved and particulate selenium. They have been used by many other labs, including the US Geological Survey, for selenium studies. They have been published in the peer-reviewed scientific literature (Cutter, 1978, 1982, 1983, 1985; Velinsky and Cutter, 1990).

Task 2. Preparation of Status Reports

Two status reports and associated requirements are specified in Table 4 under Task 3. The compliance dates are February 1, 2011 and February 1, 2012. The results of the first and second year's sample collections will be provided to the Regional Board along with the status reports. The status report will include a preliminary review of the results, comparison and evaluation against the existing data (including the new RMP data 2006–2010) and recommendations regarding the need for changes to the current monitoring strategy.

Task 3. Preparation of Final Study Report

The final report will be provided to the Board by the August 2012 deadline. The final report will provide a detailed summary and analysis of the sampling data. These results will be augmented with updated modeling outputs using the ECoS framework developed for the North San Francisco Bay Selenium TMDL. The ECoS model was calibrated with existing data and used to predict the response to a series of load reduction scenarios. One of the objectives of the sampling effort is to verify that the values for dissolved and particulate Se concentrations used in the model calibration are appropriate. The results of the data analyses presented in the final report will be used to conduct this verification. If it is deemed that the previous values for the calibration were not appropriate, the model will be recalibrated with the new values for the boundary conditions. The new sampling data will be compared with the modeling results to address a second objective of the Se Characterization Study: to compare the dissolved and particulate Se concentrations predicted by the model with the measured values.

Specific items that will be addressed in the final report include the requirements for Task 4, elements "a" through "f" as prescribed in Table 4 of the Order (below).

- a) Sampling results, data interpretation, and conclusions, such as receiving water and mixing zone characterization, seasonal variability, etc. All sampling data will be presented and provided in electronic format.
- b) Effluent characterization. The monthly effluent samples and the receiving-water samples will provide new data on the dissolved and particulate concentrations of the discharged

selenium. These data will be used to assess the relative contribution of the refineries to the total dissolved and particulate loads to the Bay.

- c) Determination if there is reasonable potential for selenium in the discharge to violate the Basin Plan's narrative bioaccumulation objective through the use of pertinent models. The ECoS model will be used to assess the effect of a range of Se concentrations measured in the effluent and receiving water on bioaccumulation.
- d) Comparison of near-field selenium water column concentrations to applicable numeric objectives. The sampling results will provide the ability to make direct comparisons to both dissolved and particulate Se concentration objectives.
- e) Demonstration of spatial and temporal extent to which the objectives and other relevant guidelines, are being exceeded. The new sampling results will provide new information on both dissolved and particulate Se concentrations that have not been available for over ten years. These data will provide a broad spatial summary of dissolved and particulate concentrations in the Bay.
- f) Determination whether selenium levels impact foodweb and wildlife and/or contribute to bioaccumulation. The ECoS model (which includes a bioaccumulation module) will utilize the new data to demonstrate how changes in particulate Se speciation will affect bioaccumulation.

2 Schedule

The planned schedule is shown in Table 3 (below). As indicated in the task descriptions above, a series of key meetings and deliverables associated with the development and approval of the Plan are specified. The key milestones in the schedule are:

- Sampling events, shown here to targeted within 2-month windows during the dry and wet seasons in 2010, 2011, and 2012
- Preparation of the required annual status reports (February 1, 2011 and February 1, 2012)
- Preparation of the Final Study Report (August 15, 2012)

The two-year project schedule will commence on June 7, 2010 and end with the submittal of the final report to the Water Board on August 15, 2012.

**Table 3
Study Schedule**

Task	Date
Study Plan Submittal & Approval by the Board	
Draft Study Plan Submitted to the Board	June 7, 2010
WSPA/Tetra Tech Meeting with Board to Finalize Study Plan	July 8, 2010
Final Study Plan and QAPP Approved by the Board	July 15, 2010
Task 1. Conduct Sampling and Analysis	
Sampling event	Beginning September 8, 2010
Sampling event	February 1 – March 31, 2011
Sampling event	August 1 – September 30, 2011
Sampling event	February 1 – March 31, 2012
Task 2. Preparation of Status Reports	
Submit Status Report 1 to Water Board	February 1, 2011
Submit Status Report 2 to Water Board	February 1, 2012
Task 3. Preparation of Final Study Report	
Final Study Report to Water Board	August 15, 2012