# ROR016 PSSEP

PSSEP
Partnership for Sound Science in Environmental Policy

January 14, 2013

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Delta Stewardship Council
980 Ninth Street, Suite 1500
Sacramento, CA 95814

*via email to: recirculateddpeircomments@deltacouncil.ca.gov*

Re: Draft Programmatic Environmental Impact Report, Vol. 3, Recirculated Draft Delta Plan (State Clearing House # 2010122028)

Dear Ms. Messer:

These comments are submitted on behalf of the Partnership for Sound Science in Environmental Policy ("PSSEP") on the Draft Programmatic Environmental Impact Report, Vol. 3, for the Recirculated Draft Delta Plan ("RDPEIR"). PSSEP is an association of municipal and industrial entities and trade associations in California whose members are regulated by the State and Regional Water Boards under their joint, Federal Clean Water Act and Porter-Cologne Water Quality Control Act authorities. Some of PSSEP's members are located in the San Francisco Bay Area and will be directly affected by any actions taken, or decisions made by, the Delta Stewardship Council under the Final Delta Plan to be adopted thereby. As such, PSSEP and its members are "interested parties" for purposes of the California Environmental Quality Act ("CEQA"). ROR016-1

The foci of these comments are related to the unquestionable impacts that the Project (as defined in the RDPEIR) will have on the Delta and to San Francisco Bay related to a reasonably certain increase in selenium loadings that will occur from the San Joaquin River. Our exhaustive review and analysis of the RDPEIR reveals that these impacts are not even identified, let alone adequately considered, in the RDPEIR. As such, the RDPEIR cannot legally support adoption of the Recirculated Draft Delta Plan ("RDDP") unless and until adequate consideration of these impacts has been completed and fully mitigated in any final Delta Plan.

The Central Valley Regional Water Board has completed three different selenium TMDLs in its region, including the San Joaquin River Selenium TMDL (August 2001), Selenium TMDL for Grasslands Marshes (April 2000), and the Salt Slough Selenium TMDL (January 1997). All of the waters impaired by selenium and which required development of these TMDLs drain into the main-stem or tributaries of the San Joaquin ROR016-2

## *Response to comment ROR016-1*

Comment noted.

## *Response to comment ROR016-2*

This comment assumes significant new diversions of water from the Sacramento River north of the current state and federal pumping facilities and a resulting increase in flow to the Delta from the San Joaquin River, with resulting increases in selenium loads. The Delta Plan does not direct such a change in diversions or flows, nor does the EIR analyze resulting impacts on the environment. See Master Response 1. In addition, the EIR does address selenium. Subsection 3.3.4.2.2 of the Draft Program EIR discusses surface water quality in the San Joaquin watershed, including selenium. Other subsections also address the presence and sources of selenium in the Delta and its watershed (see, e.g., DEIR, pp. 3-11, 3-18, 3-37). In addition, Impacts 3-1a, 3-1c, and 3-1d address potential impacts of the Delta Plan on water resources that relate to selenium. For example, the analysis of impact 3-1a states that operation of new water supply facilities may create long-term changes in local mixtures of source waters within channels, as well as long-term changes in the balance of sedimentation and scour within channels. These changes may affect the bioavailability of pollutants, including selenium. Mitigation Measure 3-1 on page 3-93 of the Draft Program EIR also has been amended by adding the following provision: "Projects that may affect drainage patterns or flow patterns, water quality, or groundwater elevations or quality, should use appropriate and available scientific and engineering tools and methods to evaluate how operation of the project could affect Delta flow patterns, water quality, and groundwater elevation and quality. The following elements should be considered by the lead agency when pursuing a covered action: changes in hydrodynamics, timing and quantity of fresh water flow, temperature, salinity, selenium, dissolved oxygen, turbidity, nutrients, methylmercury, and total organic carbon loadings and/or concentrations."

River. The San Joaquin River, in turn, flows into the Delta and, ultimately, through San Francisco Bay. It is therefore not an overstatement to say that ***virtually all*** of the selenium loading from the San Joaquin River has a quantifiable and likely significant impact on selenium loading to the San Francisco Bay.

The San Francisco Regional Water Board began work on a selenium TMDL for North San Francisco Bay in 2007. Since that time, numerous studies have been completed to analyze the contribution of selenium coming from the Delta, including loads derived from the Sacramento River and the San Joaquin River. Total selenium loads to San Francisco Bay from the Delta have been estimated at approximately 3,938 kg/year. (Technical Memorandum 2: North San Francisco Bay Selenium Data Summary and Source Analysis. Table 3-19, p. 3-60. July 2008. TetraTech, Inc., http://www.swrcb.ca.gov/rwqcb2/water_issues/programs/TMDLs/northsfbayselenium/TMDL_TM2_July2008.pdf). The estimated selenium contribution from the Sacramento River at Freeport is 1,577 kg/yr, and the estimated selenium contribution from the San Joaquin River at Vernalis is 2,289 kg/yr. ROR016-2

Any project or program that encourages, leads to, or results in a hydrologic change that extracts water from the Sacramento River north of the existing Federal and State Water Projects pumping facilities near Tracy will mean that ***more*** water from the San Joaquin River will necessarily flow into the Delta and impact San Francisco Bay. This, in turn, will likely have dramatic and substantial impacts on selenium loadings from the Delta into San Francisco Bay. As a result thereof, logic dictates that there will be substantial impacts on fish and other wildlife in San Francisco Bay. This phenomenon was recently explored by scientists studying the sources and fate of selenium loads affecting San Francisco Bay, wherein it was concluded that, "Manipulations to the Delta system, especially those that increase San Joaquin [River] flow into the bay, will also have selenium impacts to the bay that must be evaluated." ("*Modeling Fate, Transport, and Biological Uptake of Selenium in North San Francisco Bay*", L. Chen, Meseck, Roy, Grieb, and Baginska; Estuaries & Coasts, November 2012.)

Current BDCP implementation projects include the construction and operation of five intake structures on the east bank of the Sacramento River between Clarksburg and Walnut Grove, each with a water diversion capacity of 3,000 cubic feet per second (cfs). The water extracted from the Sacramento River from these five intake structures would then travel in pipelines from the intakes to a sedimentation basin and solids lagoon before reaching the intake pumping plants. From the intake pumping plants water will be pumped into another set of pipelines to an Intermediate Forebay (via a transition structure) or to a tunnel (Tunnel 1) that would also carry water to the Intermediate Forebay. From this forebay, water would be pumped or conveyed by a gravity bypass system into a dual-bore tunnel (Tunnel 2) that will run south to a new ROR016-3

## *Response to comment ROR016-3*

The proposed BDCP is a reasonably foreseeable future project that is not part of the Delta Plan. It is being evaluated by the Department of Water Resources as the CEQA lead agency. The cumulative impacts of the proposed Delta Plan, in combination with the impact of the proposed BDCP, are described in EIR Sections 22 and 23. Please refer to Master Response 1.

forebay near Byron Tract, adjacent to Clifton Court Forebay. (http://baydeltaconservationplan.com/Libraries/Dynamic_Document_Library/BDCP_Chapter_4_-_Covered_Activities_and_Associated_Federal_Actions_2-29-12.sflb.ashx) Thus, the currently-envisioned BDCP implementation project(s) would result in a massive amount of Sacramento River water being removed from the Delta, resulting in a substantial increase in flow from the San Joaquin River, along with what is already known to be extremely elevated levels of selenium.

A review of the BDCP technical documents purporting to analyze potential impacts associated with increased San Joaquin River selenium loading to the Delta fails in at least two respects. (*See*, Appendix D (Toxins) of the Bay Delta Conservation Plan, Working Draft (January 2012).) First, the BDCP analysis of potential selenium impacts is focused ***solely*** on potential impacts to the Delta and Suisun Bay, and is ***completely void*** of any analysis on potential impacts of selenium loads to San Francisco Bay. This obviously fails to satisfy CEQA. ROR016-3

Second, the BDCP selenium analyses findings presented in Table D-21 were that preliminary proposal actions (we assume this means flow scenarios) would result in a less than 10% annual average increase in San Joaquin River water in the south Delta relative to other source waters (including the Sacramento River). The preliminary proposed actions were determined to have little to no effect on the proportion of San Joaquin water flows to Suisun Marsh. While the selenium issue is addressed in the working draft document, very few details are provided, and we have numerous questions and concerns regarding the modeling details and the aqueous selenium concentrations findings presented in Appendix D. For example, the historical selenium concentrations presented for the Sacramento River in Table D-14 are very high compared with what many researchers have measured. Also, the predicted concentrations for all locations in Table D-15 are very high. It seems that the lack of concern with the predicted selenium concentrations as well as the overall assessment approach by BDCP is based on demonstrating the ability to meet the "lowest of relevant thresholds", *i.e.*, 2 ug/L, the level of concern for the Grassland Bypass Project. We question whether DSC and BDCP staff have been in contact with USGS and USEPA to ascertain what the revised selenium criterion for San Francisco Bay is likely to be, and how that criterion may affect the assumptions made in the RDPEIR and underlying BDCP work in this area.

Section 3 of the RDPDEIR generally discusses "project level" water quality impacts associated with construction and operation of various unidentified "facilities" that would be "encouraged" by adoption of the Delta Plan. These impacts also generally relate to potential water quality impacts ***within*** the Delta associated with construction and operation of these unidentified facilities. And while we appreciate the ROR016-4

## *Response to comment ROR016-4*

Because the Delta Stewardship Council cannot direct the construction of specific projects, nor would the projects be implemented under the direct authority of the Council, it is difficult to identify specific future projects, including their location. Due to this uncertainty and the programmatic nature of the EIR in the absence of project-specific information, it is not appropriate to speculate regarding details of future project-specific impacts. Analyses associated with specific projects will provide such project-level details as they become available. See also Master Response 2.

ROR016-4

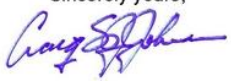
fact that, "Project-level impacts would be addressed in future site-specific environmental analysis conducted at the time such projects are proposed by lead agencies," CEQA mandates that all reasonably known impacts of the programmatic project be identified, analyzed, and where deemed substantial, adequately mitigated.

We have thoroughly analyzed the RDPEIR and have found no discussion of the selenium-related issues or impacts referenced in this comment letter. This is despite the fact that much of the information on which these comments are based has been known to various agencies that have coordinated with the Delta Stewardship Council in developing the draft Delta Plan for at least three years. In any event, we respectfully request that the RDPEIR be amended to reflect these concerns, and to adequately address the potentially substantial water quality impacts associated with any anticipated "manipulations to the Delta system" as Chen, *et al* have observed. Equally important is the need for the RDPEIR to identify adequate mitigation measures for the likely impacts, along with a reasonable estimate of, and the source of funding for, implementation of those mitigation measures.

ROR016-5

Thank you for the opportunity to provide these comments.

Sincerely yours,



Craig S.J. Johns
Program Manager

Attachments:

(1) Technical Memorandum 2: North San Francisco Bay Selenium Data Summary and Source Analysis, July 2008, TetraTech, Inc.

(2) *"Modeling Fate, Transport, and Biological Uptake of Selenium in North San Francisco Bay"*, L. Chen, Meseck, Roy, Grieb, and Baginska; Estuaries & Coasts, November 2012.

(3) "Working Draft. Bay Delta Conservation Plan, Appendix D: Toxins", ICF International. January, 2012.

## *Response to comment ROR016-5*

Please see response to comment ROR016-2.

1115 – 11th Street, Suite 100 * Sacramento, CA * 95814 * 916/498-3326

*No comments*

- n/a -

***No comments***

- n/a -

# TECHNICAL MEMORANDUM 2: NORTH SAN FRANCISCO BAY SELENIUM DATA SUMMARY AND SOURCE ANALYSIS

**July 2008**

Prepared for:
Regional Water Quality Control Board
San Francisco Bay Region
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Prepared by:
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## *No comments*

- n/a -

## 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 |



***No comments***

- n/a -

## *No comments*

- n/a -

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## *No comments*

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## No comments

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***No comments***

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## *No comments*

- n/a -

## 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



***No comments***

- n/a -

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.



## No comments

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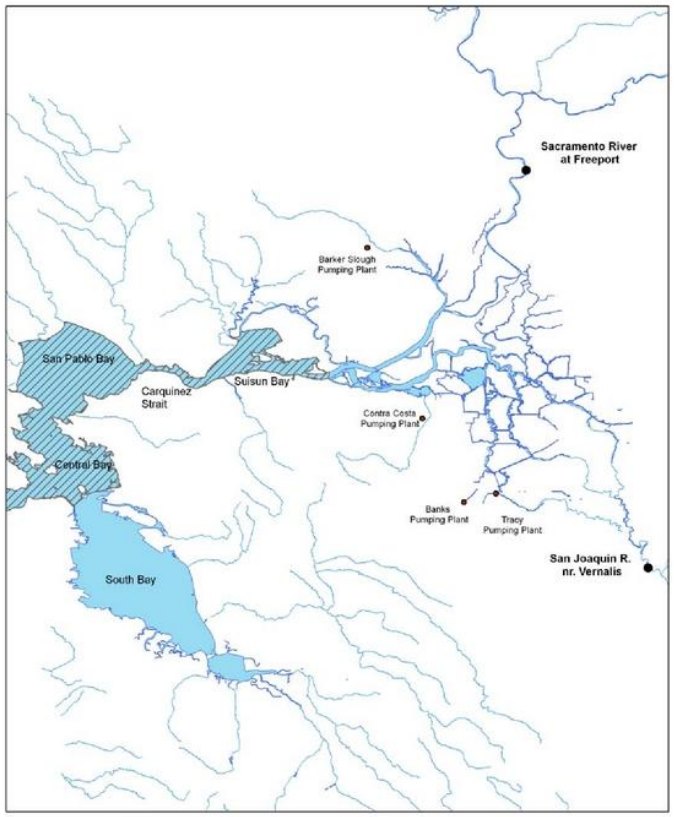


**Figure 1-1** **The San Francisco Bay estuary, Delta and Sacramento and San Joaquin Rivers. The cross-hatched area shows the area of interest for the North San Francisco Bay Selenium TMDL. The Sacramento River at Freeport and the San Joaquin River at Vernalis are the principal freshwater inflows into the Delta. A significant portion of the freshwater inflows are exported out of the Delta through the four pumping plants shown.**



## *No comments*

- n/a -

## *No comments*

- n/a -

## 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 University[1]. 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.[1]

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).



***No comments***

- n/a -

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 along side 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



## No comments

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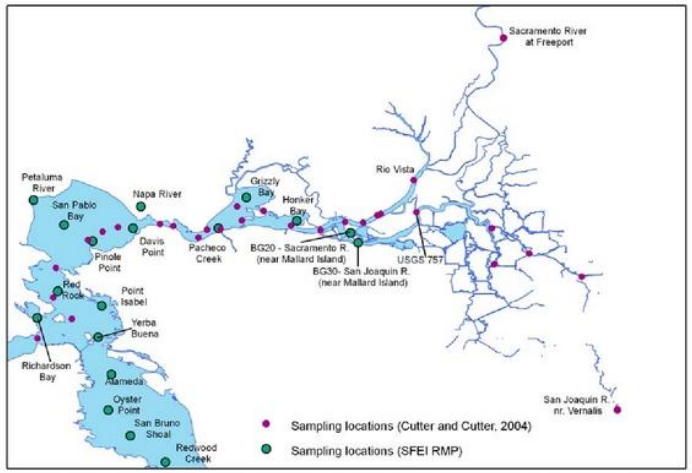


**Figure 2-1** **Locations of RMP long-term monitoring sites and sampling by Cutter and Cutter (2004) during November 1999.**

## 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 µg/L and 0.13-0.24 µg/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 µg/L (0.03-0.24 µg/L, n = 105 ) and 0.13 µg/L (0.04-0.45 µg/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 µg/L (range: 0.03-0.44 µg/L, n = 258) and 0.20 µg/L (0.02-0.5 µg/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.



## *No comments*

- n/a -

**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 (µg/L) | S.D. (µg/L) | Median (µg/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



## *No comments*

- n/a -

**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



## *No comments*

- n/a -

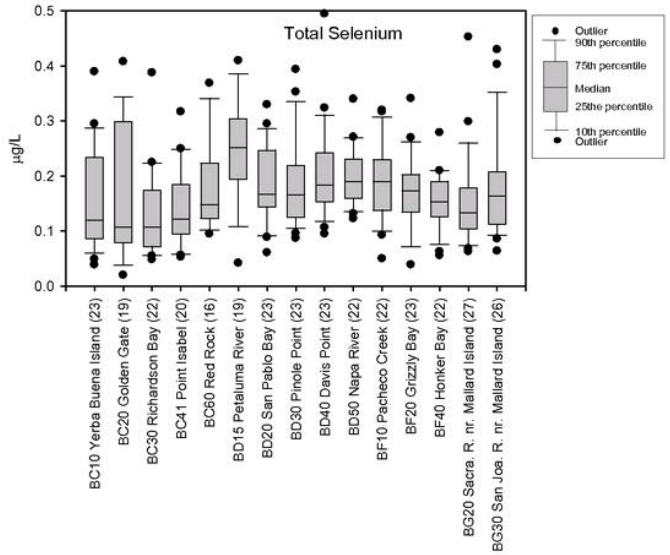


**Figure 2-2** **Total selenium concentrations at long-term monitoring sites for the period of 1993-2005. Values in parentheses are numbers of samples (data source: RMP).**

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.



## *No comments*

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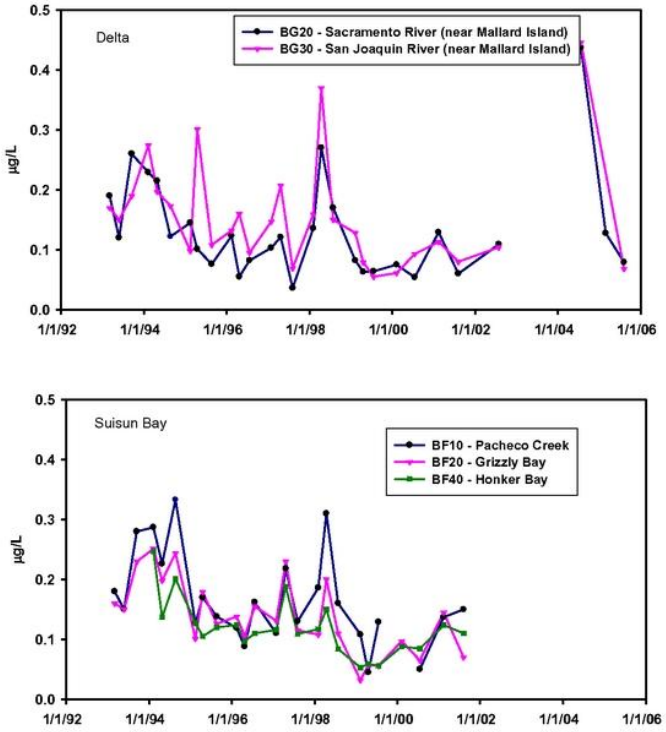


**Figure 2-3** **Dissolved selenium concentrations as a function of time in stations near Mallard Island and in Suisun Bay (data source: RMP).**



## *No comments*

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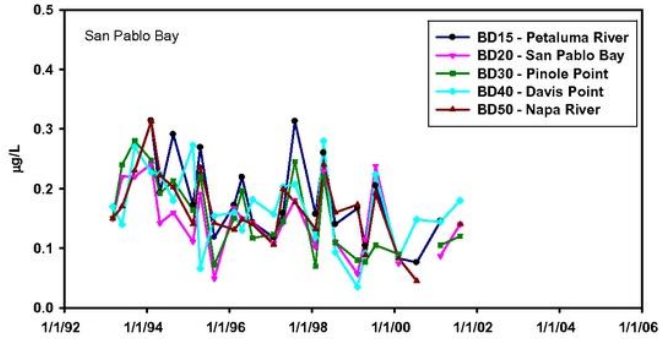


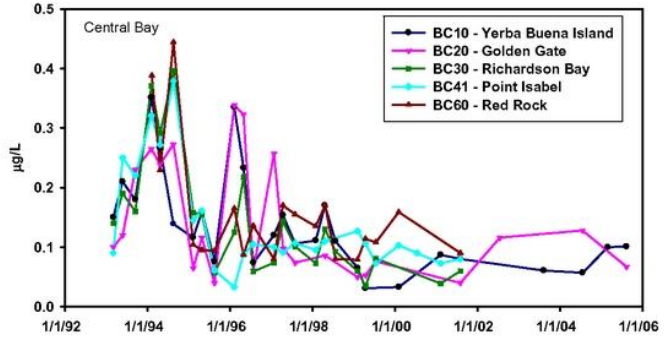


**Figure 2-4** **Dissolved selenium concentrations as a function of time in the San Pablo and Central Bay (data source: RMP).**



## *No comments*

- n/a -

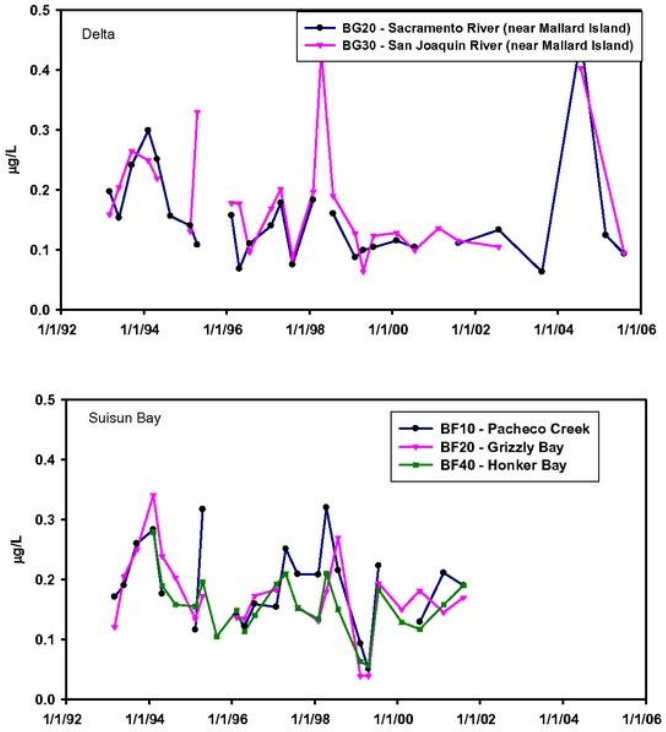


**Figure 2-5** **Total selenium concentrations as a function of time in stations near Mallard Island and in Suisun Bay (data source: RMP).**



## *No comments*

- n/a -

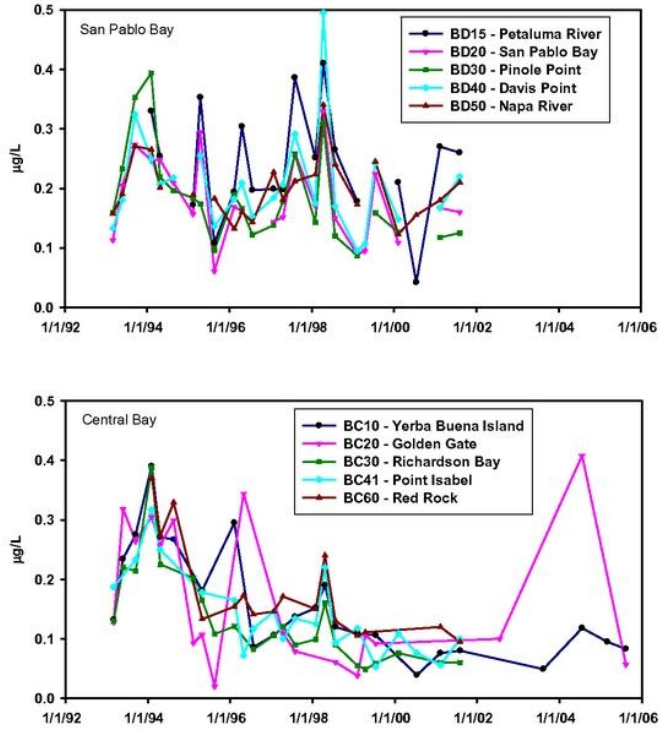


**Figure 2-6** **Total selenium concentrations as a function of time in the San Pablo and Central Bay (data source: RMP).**

## 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.



***No comments***

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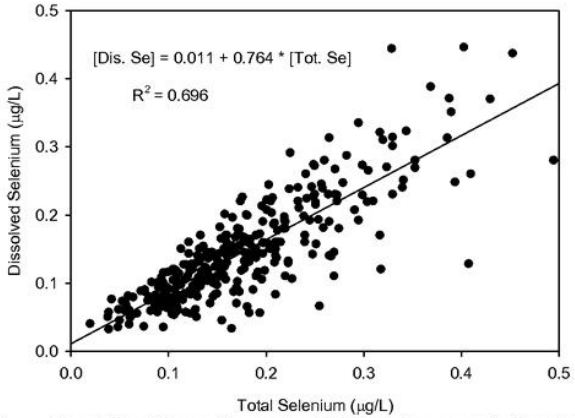


**Figure 2-7** **Correlation between dissolved and total selenium concentrations for long-term monitoring sites (data source: RMP).**

## 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).



## *No comments*

- n/a -

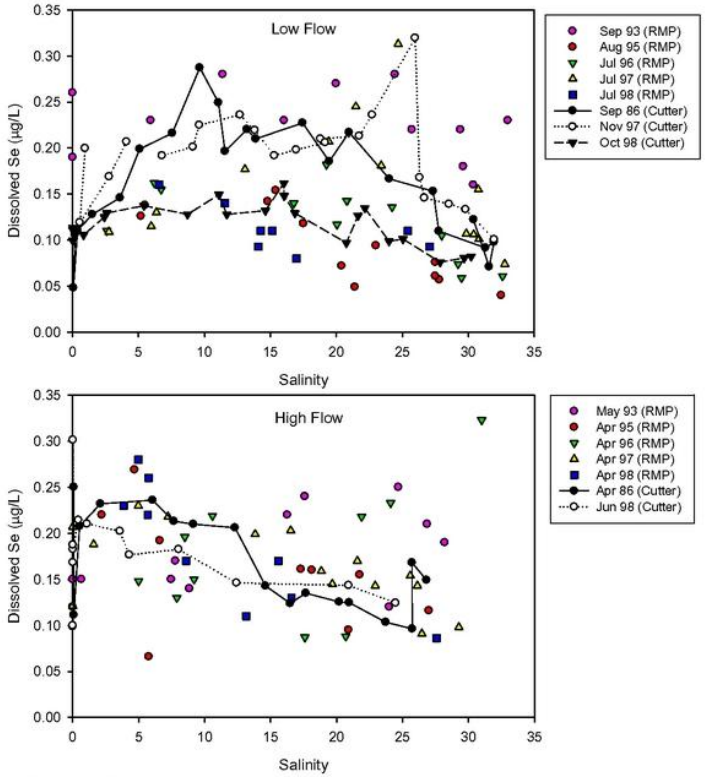


**Figure 2-8** **Dissolved selenium concentrations along salinity gradient during low and high flow sampling periods by RMP and Cutter and Cutter (2004) before 1999[2].**

[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 $10^{10}$l/d (low flow), NDOI > 8.5 x $10^{10}$l/d (high flow) with October 1998 defined as low flow for simplification.



## *No comments*

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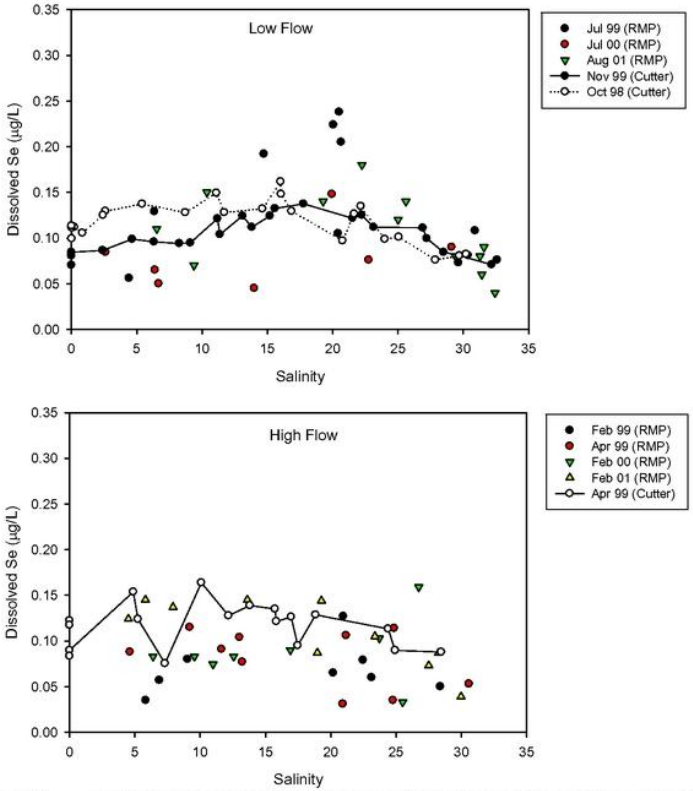


**Figure 2-9** **Dissolved selenium concentrations as a function of salinity during low and high flow sampling periods by RMP and Cutter and Cutter (2004) from 1999 onwards.**

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.



## *No comments*

- n/a -

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).

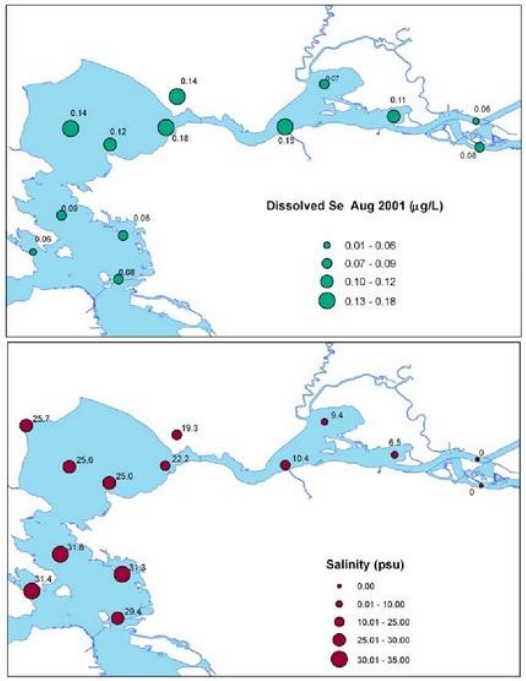


**Figure 2-10** **Spatial distribution of dissolved selenium and salinity during a sampling event in a dry period of a dry year (August 2001) by the RMP.**



## *No comments*

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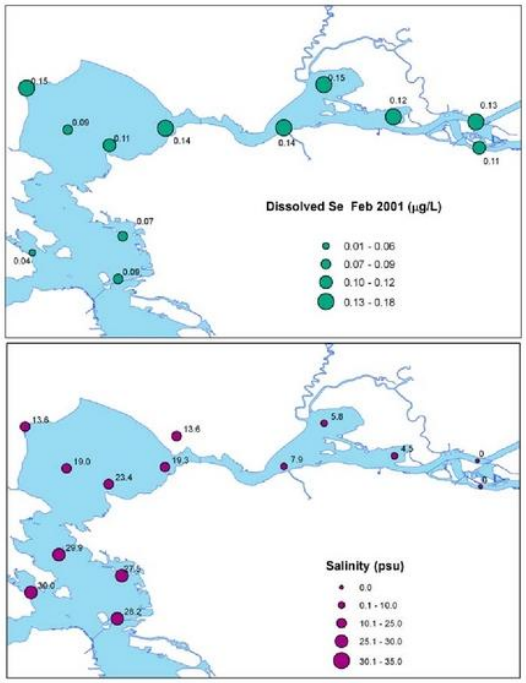


**Figure 2-11** **Spatial distribution of dissolved selenium and salinity during a sampling event in a wet period (February 2001) by the RMP.**

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



## *No comments*

- n/a -

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.



## No comments

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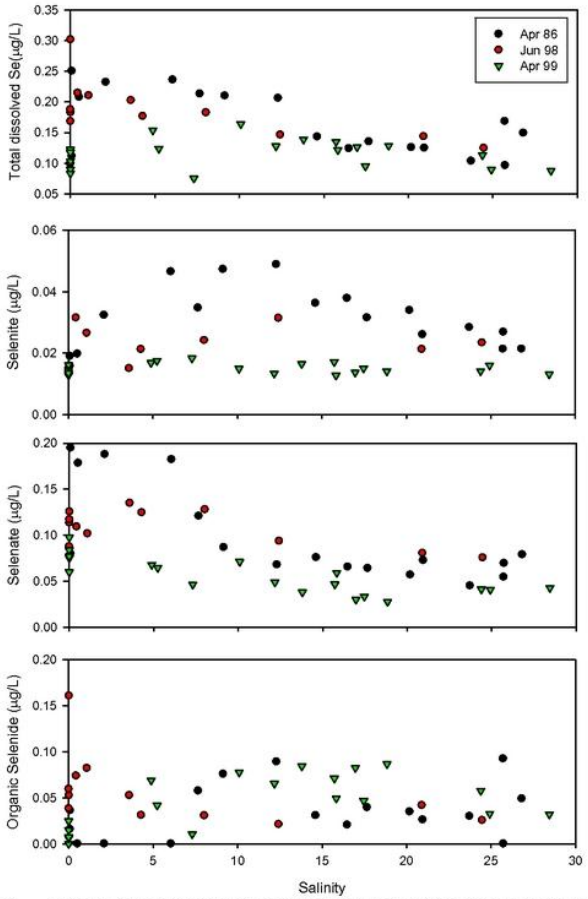


**Figure 2-12** **Transects of dissolved selenium, selenite, selenate, and organic selenide under high flow sampling periods (April 1986, June 1998, and April 1999; from Cutter and Cutter, 2004).**



## *No comments*

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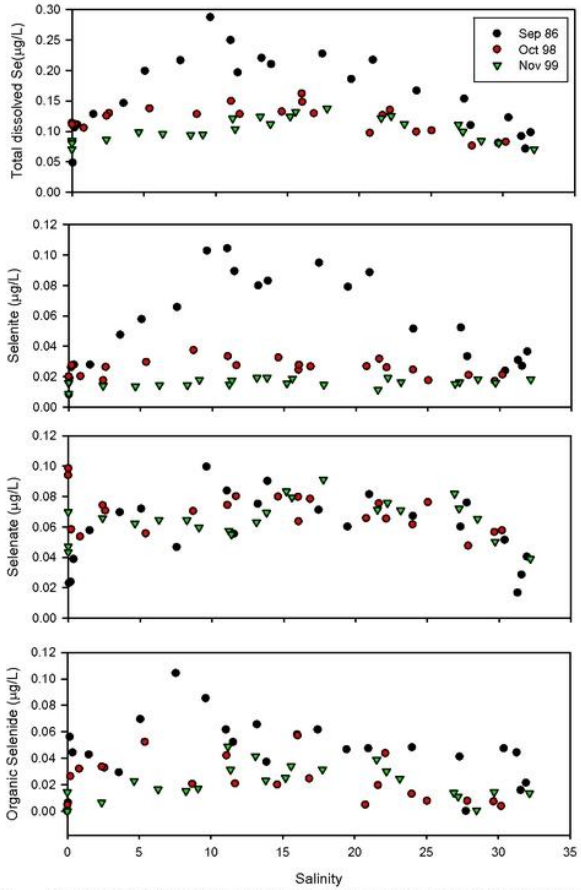


**Figure 2-13** **Transects of dissolved selenium, selenite, selenate and organic selenide under low flow sampling periods (September 1986, October 1998, and November 1999; from Cutter and Cutter, 2004).**

## *No comments*

- n/a -

## 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 |



## *No comments*

- n/a -

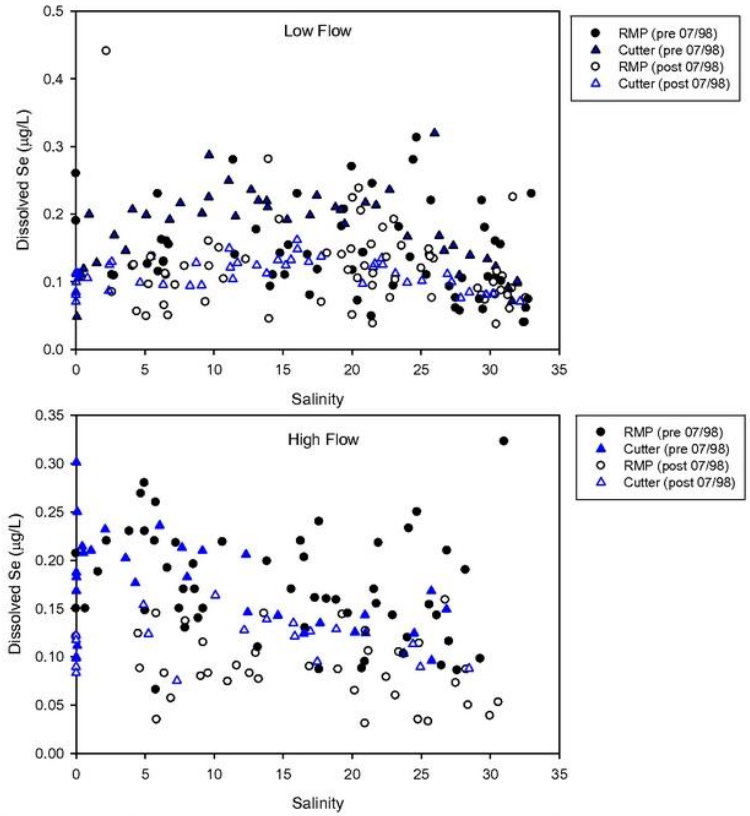


**Figure 2-14** **Dissolved selenium concentrations under low and high flow before and after July 1998 (data: RMP and Cutter and Cutter, 2004). The July 1998 cutoff date represents samples before and after improved wastewater treatment at the North Bay refineries.**



## *No comments*

- n/a -

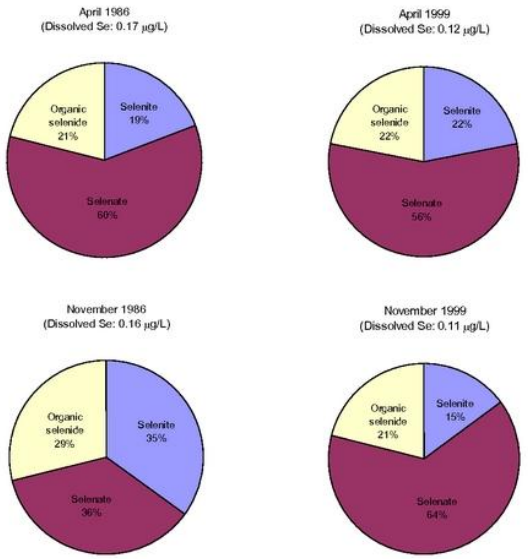


**Figure 2-15 Speciation of dissolved selenium in Bay water column during different time periods (Data: Cutter and Cutter, 2004).**

## 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 ºC and weighed for TSM concentration (Doblin et al. 2006).



***No comments***

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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 µg/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.



## *No comments*

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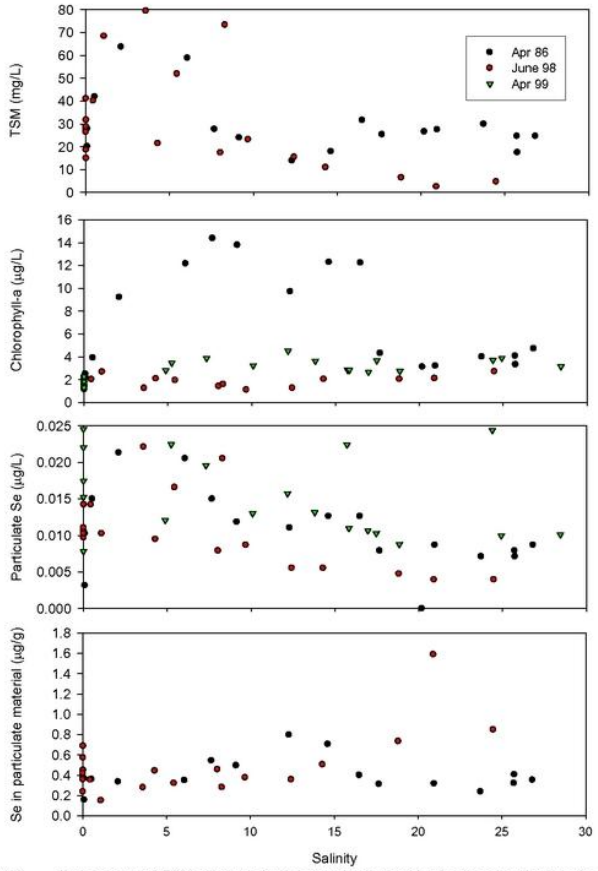


**Figure 2-16** **Transects of TSM, chlorophyll-a, particulate selenium and selenium in particulate material under high flow (April 1986, June 1998 and April 1999; Doblin et al. 2006).**



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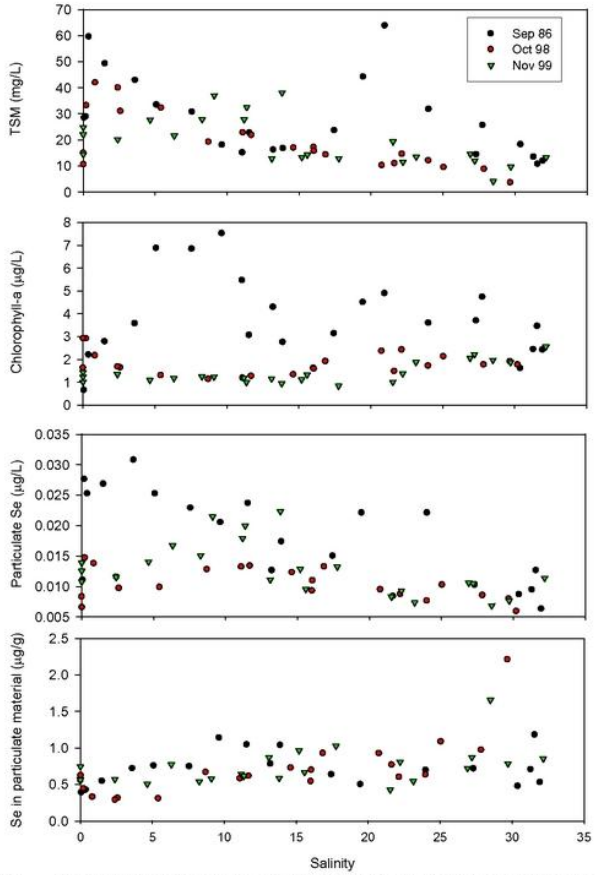


**Figure 2-17** **Transects of TSM, chlorophyll-a, particulate selenium and selenium in particulate material under low flow (September 1986, October 1998, and November 1999; Doblin et al. 2006).**

Particulate selenium concentrations, expressed as µg/l, vary less over time than TSM (Table 2-5), although selenium content in suspended particles differs between low flow and high



## *No comments*

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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 ± 27%), followed by elemental selenium (35 ± 28%), and adsorbed selenite and selenate (20 ± 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 (µg/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 (µg/g) | 0.70 ± 0.41 | 0.73 ± 0.25 | 0.87 ± 0.30 | 0.49 ± 0.31 | -- |
| Se: C ratio (X $10^{-6}$) | 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).



## No comments

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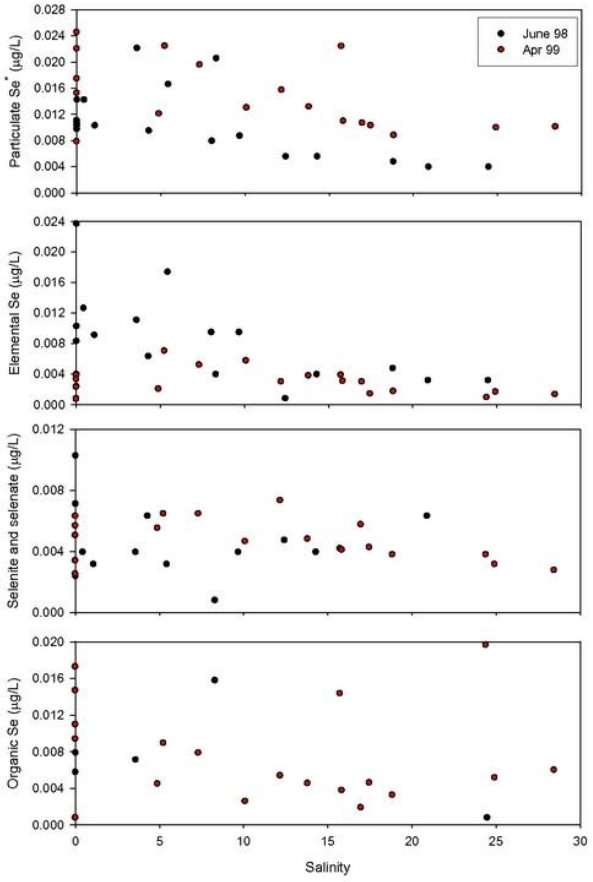


*include all adsorbed selenite and selenate, elemental and organic selenium

**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).**



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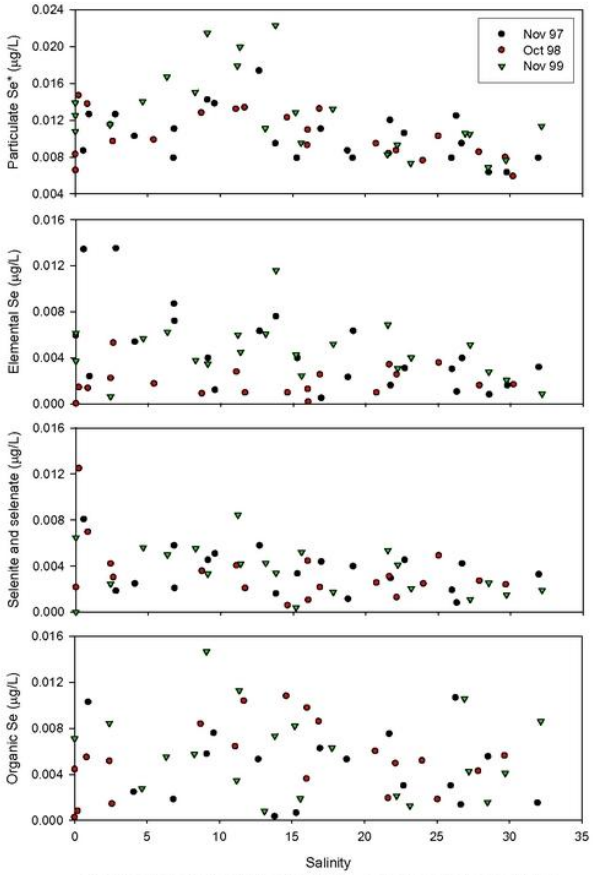


**Figure 2-19** **Transects of total particulate selenium, particulate elemental selenium, particulate adsorbed selenite and selenate, and particulate organic selenium during low flow (November 1997, October 1998 and November 1999; Doblin et al. 2006).**



## *No comments*

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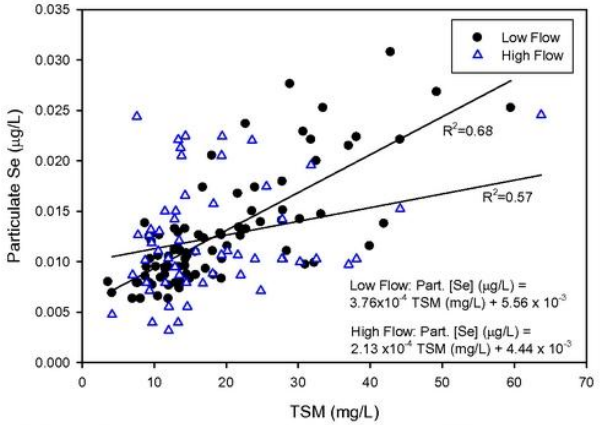


**Figure 2-20** **Correlation between particulate selenium and TSM under low and high flow (Data Source: G. Cutter, personal communication)**



## *No comments*

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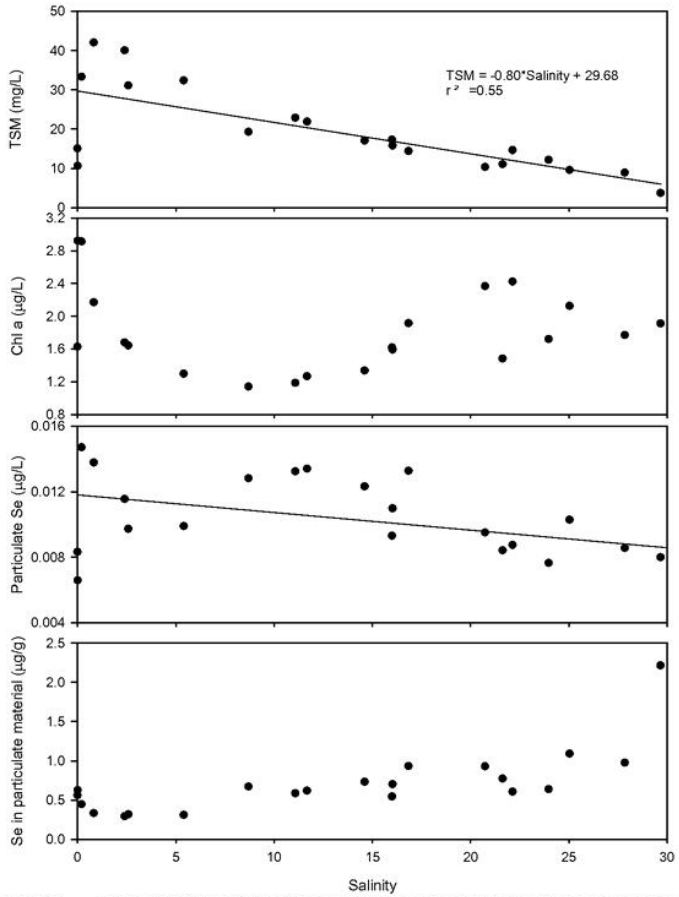


**Figure 2-21** **Concentrations of TSM, Chl a, and particulate selenium and selenium content in particulates for a low flow sampling event of Oct. 1998 (Doblin et al. 2006).**



## *No comments*

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## 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).



***No comments***

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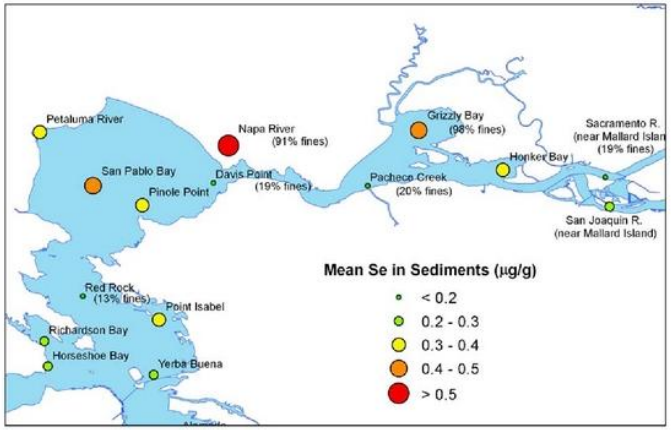


**Figure 2-22** **Mean selenium concentrations in sediments for the period of 1993-2005 (data source: RMP).**

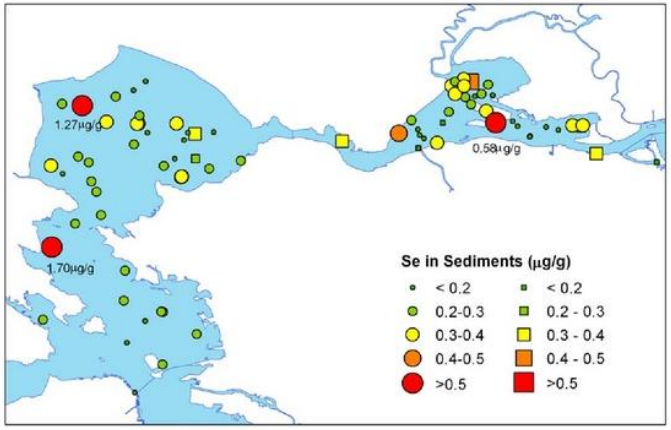


**Figure 2-23** **Selenium concentrations in sediments with data from RMP random sampling sites (circles) and data collected by G. Cutter's research group (squares). Numbers shown are individual values from the sampling.**



## *No comments*

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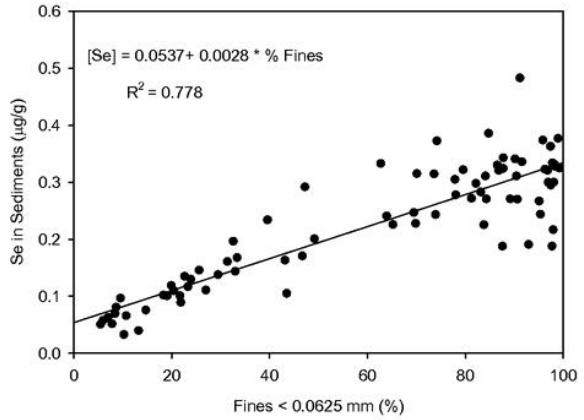


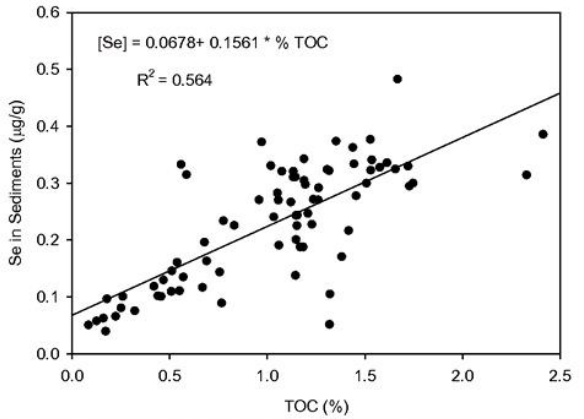


**Figure 2-24** **Relationship between selenium concentrations in sediments and sediment characteristics at long-term sites (data source: RMP).**



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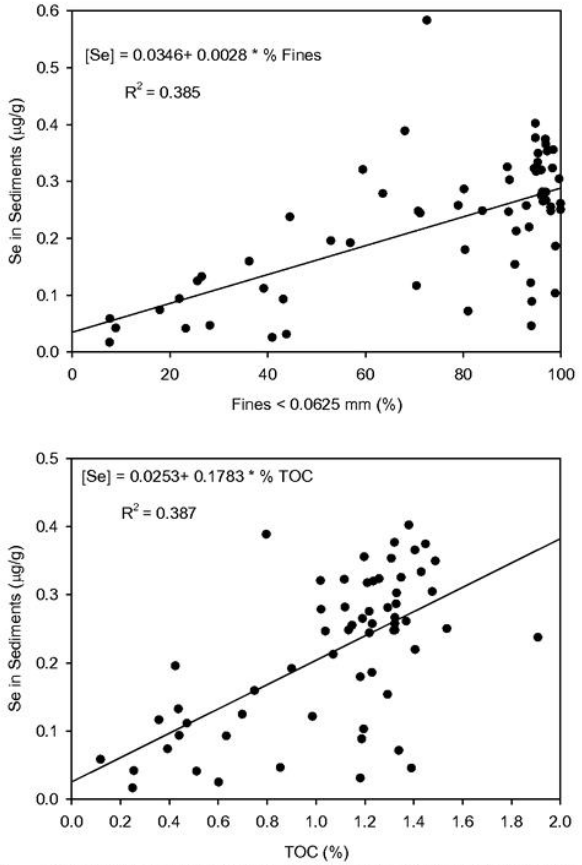


**Figure 2-25** **Relationship between selenium concentrations in sediments and sediment characteristics at random sampling sites (data source: RMP).**



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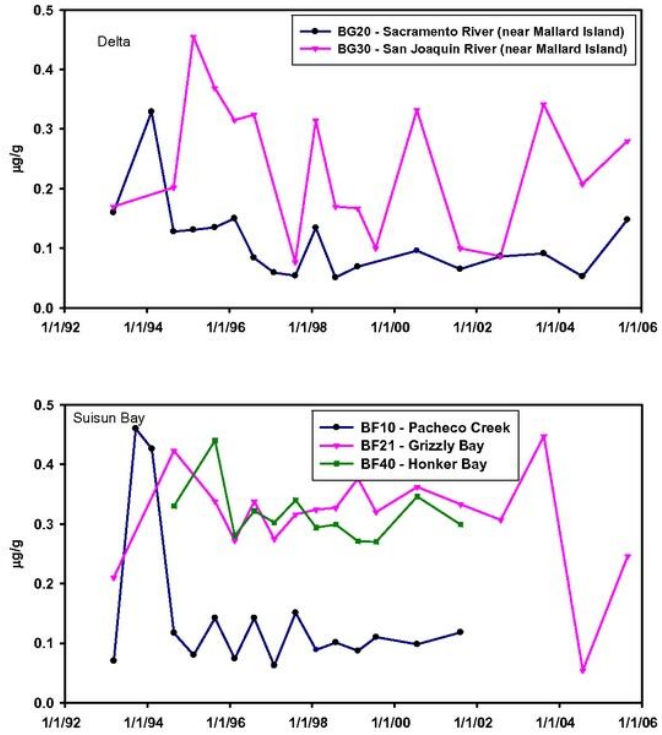


**Figure 2-26** **Selenium concentrations in sediments as a function of time in stations near Mallard Island and in Suisun Bay (data source: RMP).**



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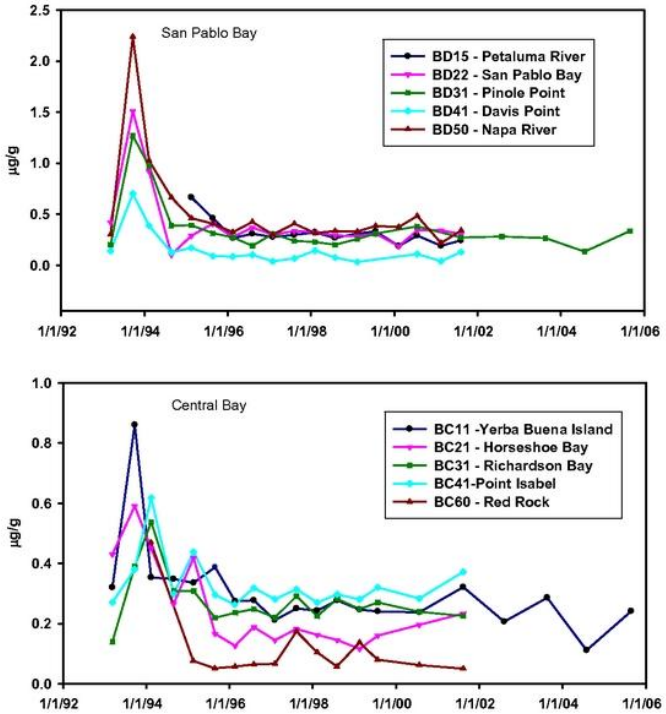


**Figure 2-27** **Selenium concentrations in sediments as a function of time in San Pablo and Central Bay (data source: RMP).**



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## 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



***No comments***

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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 $Mm^3$ (McKee et al., 2002) and annual discharge volume from wastewater is at a similar volume of 866 $Mm^3$ (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 loads 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



## No comments

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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 µm; 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 µg/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 µg/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 µg/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 (~100 $t/km^2$ vs. ~14 $t/km^2$; 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 µg/L (median 0.38 µg/L) for the dry season and 0.56-9 µg/L (median 3.6 µg/L) for the wet season (EOA, 2006). Selenium concentrations observed in five tributaries of the North Bay in the Surface Water Ambient Monitoring



## No comments

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Program (SWAMP) study in 2001-2002 suggested high concentrations of 0.18-3.39 µg/L (median 0.94 µg/L) during the dry season and 0.39- 3.14 µg/L (median 0.90 µg/L) during the wet season (SFBRWQCB, 2007a). Total selenium concentrations as high as 1.7 µg/L and 4 µg/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 SWAMP[4] 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 µg/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 µg/L at KIR115-Kirker Creek Apartments). Average total selenium concentrations for the most downstream sites of all the North Bay watersheds are 1.57 µg/L for wet season, 1.03 µg/L for spring season and 1.95 µg/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 µg/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 µg/L) and higher percentage of non-detects in early period of the study (1988-1992). Lower detection limits (generally below 0.05 µg/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.



## No comments

- n/a -

with detection limits. Land uses for watersheds surrounding the sampling locations include open forests, industrial, residential and commercial. Median concentrations are 0.40 µg/L during dry weather (n = 7) and 0.33 µg/L for storm event sampling (n = 28). By land use, median concentrations are 0.29 µg/L, 0.35 µg/L and 0.30 µg/L for residential, open and industrial sites. For some of the BASMAA sampling sties, 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 µg/L | Dissolved µg/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 |



## No comments

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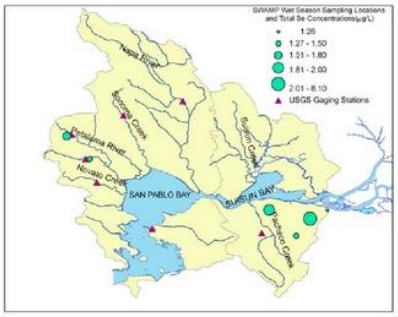
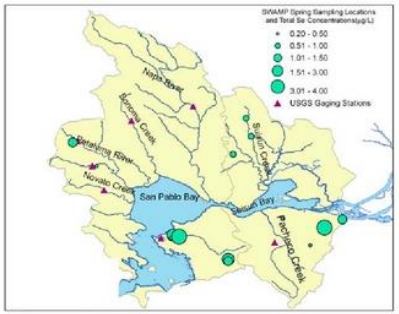
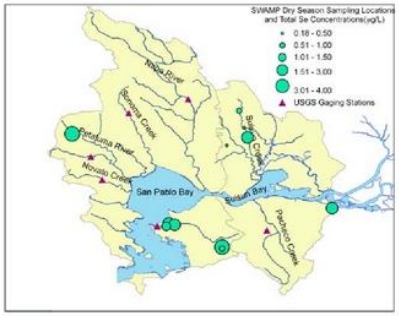



(a)




(b)




(c)

**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.**



## *No comments*

- n/a -

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.

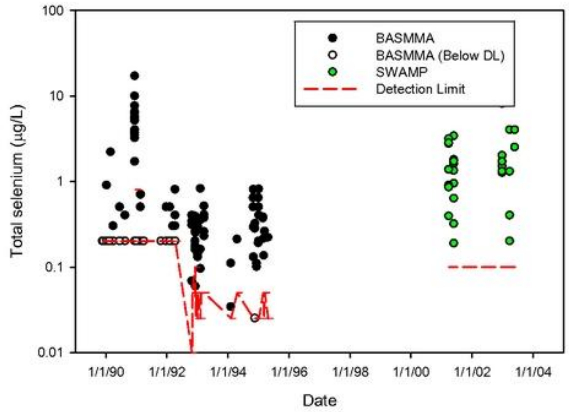



**Figure 3-2** **Total selenium concentrations in tributaries of NSFB sampled during 1990–1996 and 2000–2003 (Source: BASMAA, 1996; SWAMP data from SFBRWQCB, 2007a, b).**

### *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 (r2 = 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 (CV) ranging from 0.65 to 1.01 (McKee et al. 2002). The $10^{th}$ and $90^{th}$ 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, $10^{th}$ and $90^{th}$ percentiles of the selenium loadings were calculated to be 522.8 kg/yr and 1367.2 kg/yr, respectively.



## *No comments*

- n/a -

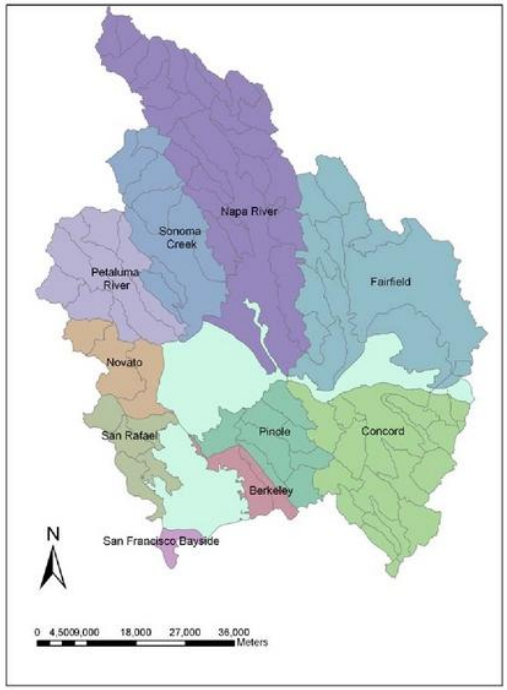



**Figure 3-3** **Hydrological areas surrounding NSFB. Source: San Francisco Estuary Institute**



## *No comments*

- n/a -

**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



## *No comments*

- n/a -

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 SWAMP 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 |



## *No comments*

- n/a -

**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)**

| | USGS11459500 (Novato Creek at Novato) | USGS11459300 (San Antonia Creek nr. Petaluma) | USGS11459000 (Petaluma River at Petaluma) | USGS11458500 (Sonoma Creek at Agua Caliente) | USGS11458000 (Napa River nr. Napa) | USGS11181400 (Wildcat Creek at Richmond) | USGS11183600 (Walnut Creek at Concord) | USGS11182100 (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 |



## *No comments*

- n/a -

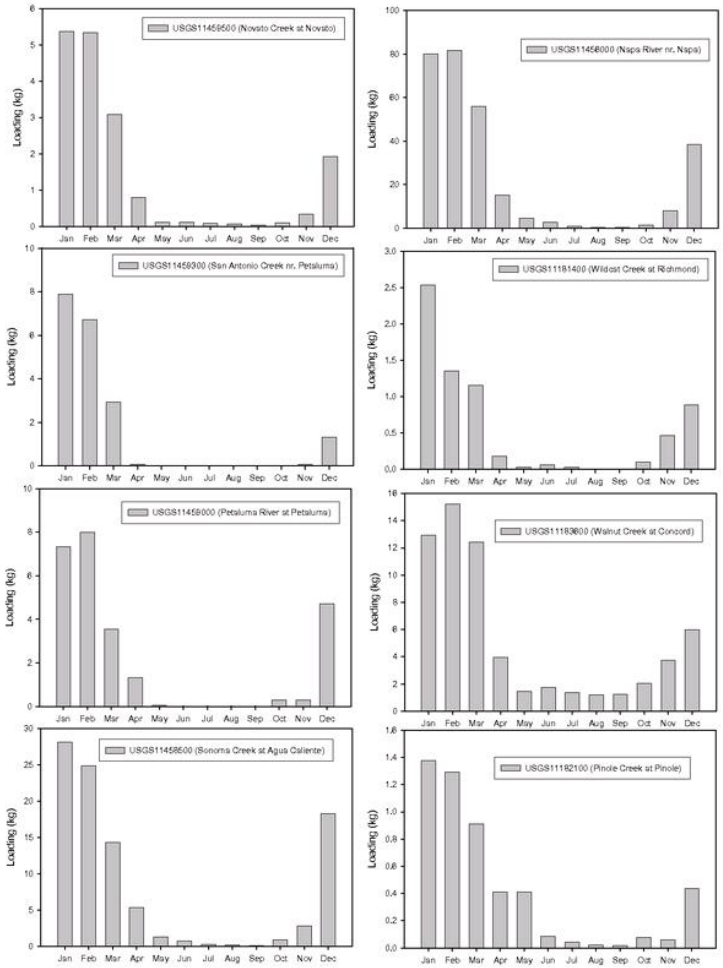



**Figure 3-4** **Estimated long-term average monthly selenium loadings at gaging stations of local tributaries.**



## *No comments*

- n/a -

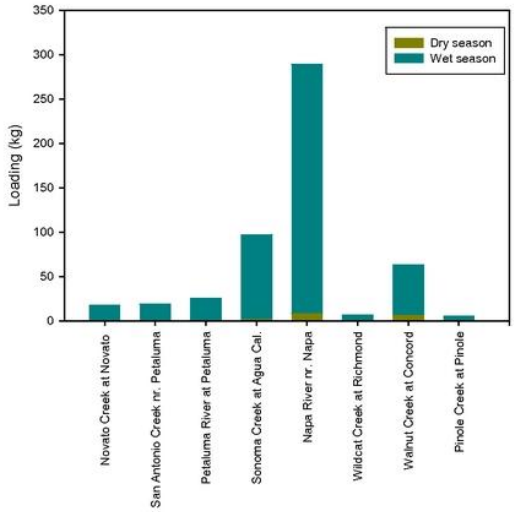



**Figure 3-5** **Comparison of dry and wet season selenium loadings for tributaries in the North Bay.**

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.



## *No comments*

- n/a -

**Table 3-5**
**Estimated long-term average monthly total selenium loadings (kg/month) to the gaging stations.**

| | USGS11459500 (Novato Creek at Novato) | USGS11459300 (San Antonia Creek nr. Petaluma) | USGS11459000 (Petaluma River at Petaluma) | USGS11458500 (Sonoma Creek at Agua Caliente) | USGS11458000 (Napa River nr. Napa) | USGS11118140 0 (Wildcat Creek at Richmond) | USGS11183600 (Walnut Creek at Concord) | USGS11182100 (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 |



## *No comments*

- n/a -

**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 |

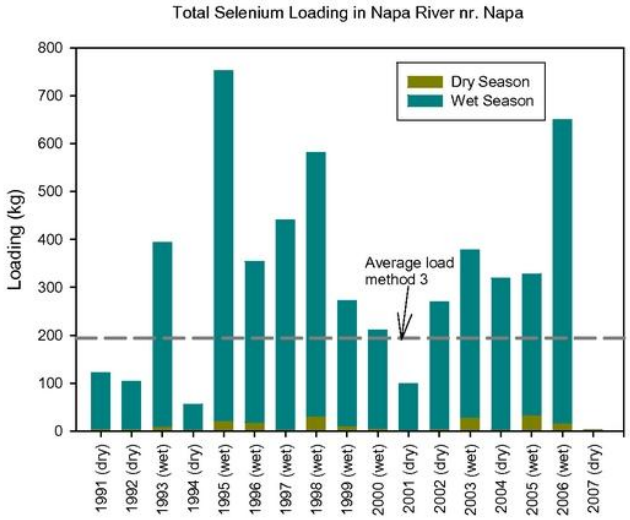



**Figure 3-6** **Dry and wet season selenium loadings by water year at Napa River near Napa.**



## *No comments*

- n/a -

### 3.3.4 Method 3: Modeled Estimates of Runoff with BASMAA and SWAMP concentrations for Calculating Land Use-Specific Loads

To estimate stormwater 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.



## No comments

- n/a -

**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) $\mu g1^{-1}$ | 0.36 | 0.58 | 0.58 | 0.50 | 0.50 | BASMAA (1996) |
| Selenium concentration (high end) $\mu g1^{-1}$ | 1.55 | 1.55 | 1.55 | 0.85 | 0.85 | SWAMP |



## *No comments*

- n/a -

**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) |

[1]Urban loads are the sum of residential, commercial, and industrial land uses.

Estimated stormwater runoff from urban areas surrounding the NSFB is 316.8 $Mm^3$/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.



## *No comments*

- n/a -

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 $1.91 \times 10^8$ 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 ± 0.20µg/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



## No comments

- n/a -

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.

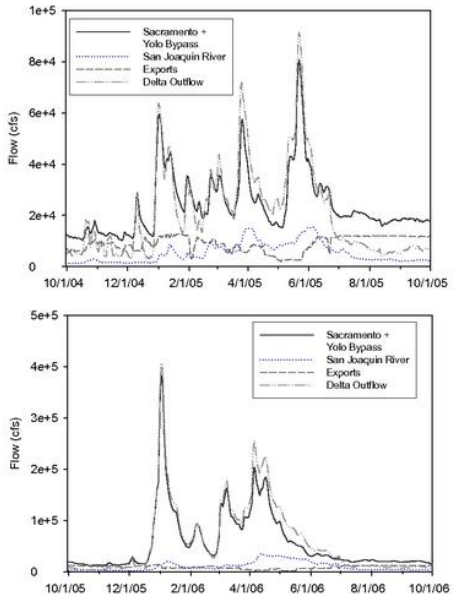



**Figure 3-7** **Flow from Sacramento River, San Joaquin River, compared to Delta exports (diversions of Central Valley Project, State Water Project, Contra Costa Water District Diversions and North Bay Aqueduct) and outflow to Delta for a dry year (water year 2004) and a wet year (water year 2005) (Data 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 µg/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 µg/l, noted above), and substantially lower than in the San Joaquin River at Vernalis (0.68 µg/l), indicating mixing between the two sources, and



## No comments

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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).



## No comments

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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 ± 0.13 µg/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 $m^3/s$), 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.



## No comments

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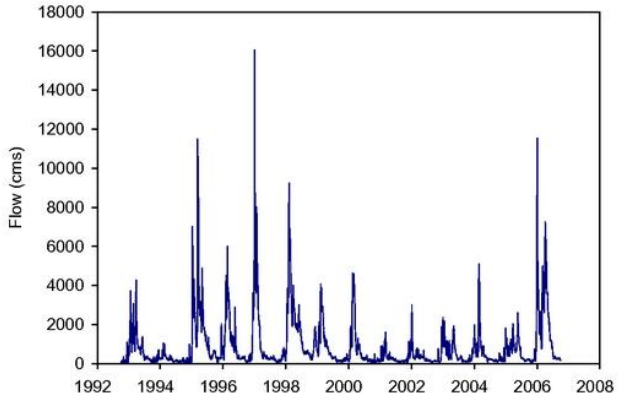


**Figure 3-8** **Daily Delta outflow for water years 1992-2006 (Data source: IEP)**

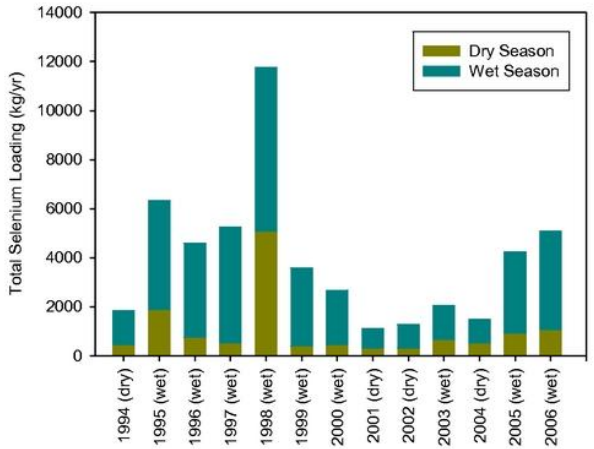


**Figure 3-9** **Estimated wet and dry season total selenium loadings from Delta to the Bay by water year.**



## *No comments*

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**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 |

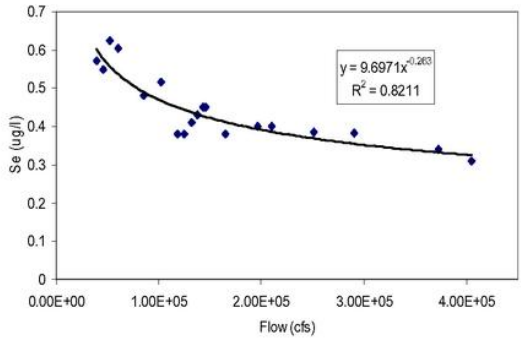


**Figure 3-10** **Relationship between total selenium concentrations and flow at Mallard Island (Data source: L. McKee).**

### *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 bases indicated relatively small changes from 1984 to 2000 (Figure 3-11). Dissolved selenium concentrations in the Sacramento River (at



## *No comments*

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Freeport) range between 0.01-0.13 µg/L, with an average of 0.07 ± 0.02 µg/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 µg/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 ± 0.20 µg/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/?referred_module=sw). The estimated daily loadings were summed to calculate the seasonal loadings. The wet season was defined as Oct 1st to Apr. 30$^{th}$ and the dry season was defined as May 1st to Sep 30$^{th}$ (Tetra Tech, 2006).



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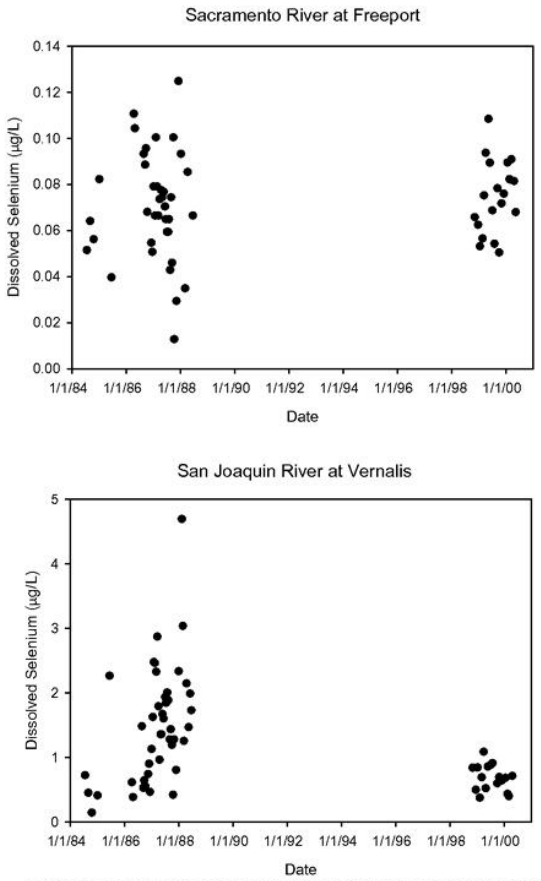


**Figure 3-11** **Dissolved selenium concentrations in Sacramento River at Freeport and San Joaquin River at Vernalis during 1984-1988 and 1998-2000, sampled by Cutter and Cutter (2004).**



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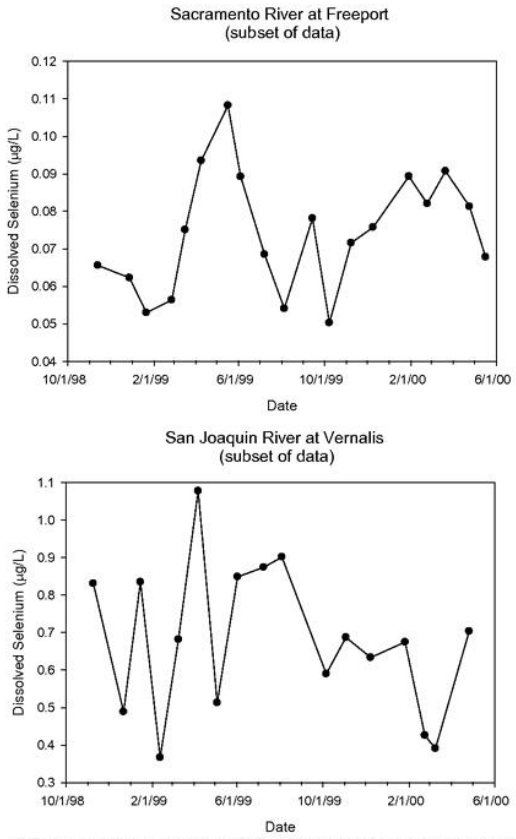


**Figure 3-12** **Dissolved selenium concentrations at Sacramento River at Freeport and San Joaquin River at Vernalis during 1998-2000, sampled by Cutter and Cutter (2004).**



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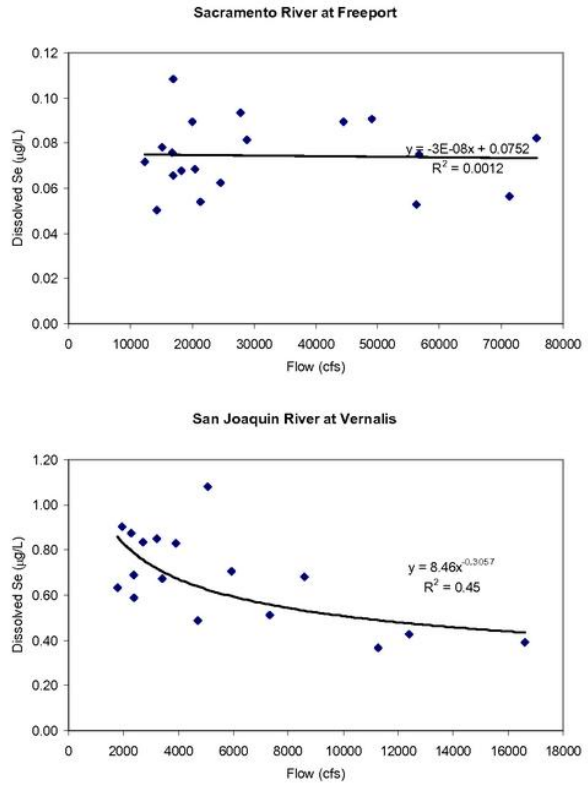


**Figure 3-13** **Relationship between dissolved selenium concentrations and daily flow for Sacramento River at Freeport and San Joaquin River at Vernalis for the period of 1998-2000 (data source: Cutter and Cutter, 2004). Note that dissolved selenium concentrations show no correlation with flow rate 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



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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 Crows 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.



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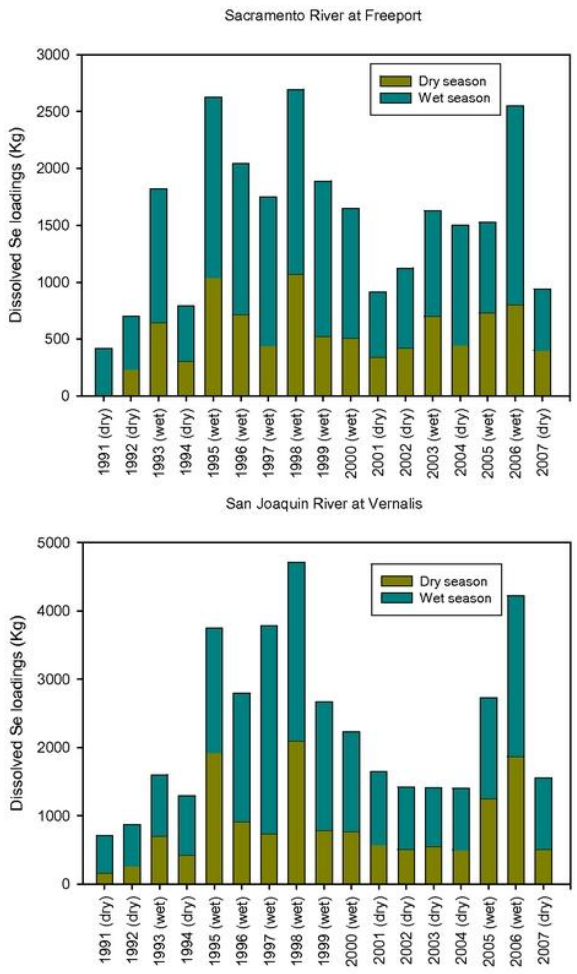


**Figure 3-14** **Dry and wet season dissolved selenium loadings at Sacramento River at Freeport and San Joaquin River at Vernalis for 1991-2007.**



## *No comments*

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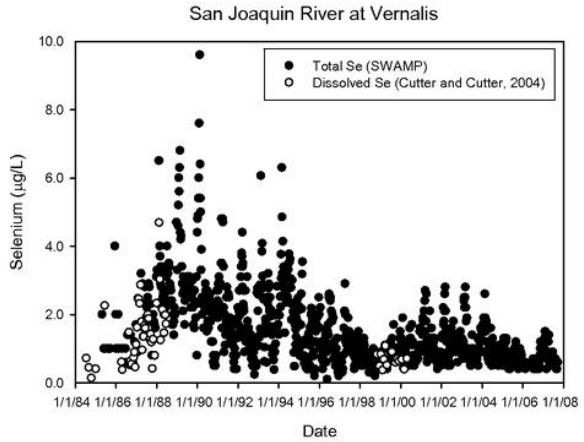


**Figure 3-15** **Dissolved selenium concentrations sampled by Cutter and Cutter (2004) at San Joaquin River at Vernalis compared to total selenium concentrations observed in SWAMP study.**

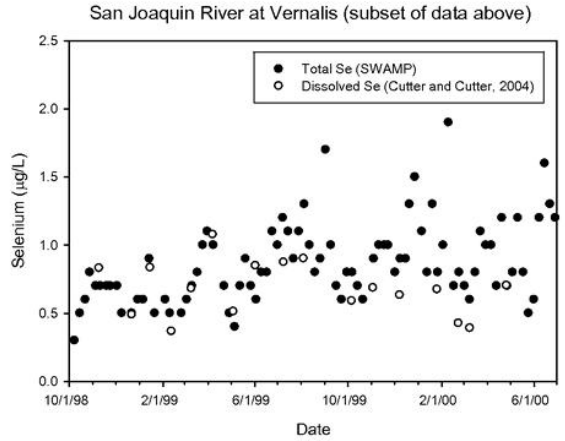


**Figure 3-16** **A subset of dissolved selenium concentrations sampled by Cutter and Cutter (2004) compared to total selenium concentrations from SWAMP.**



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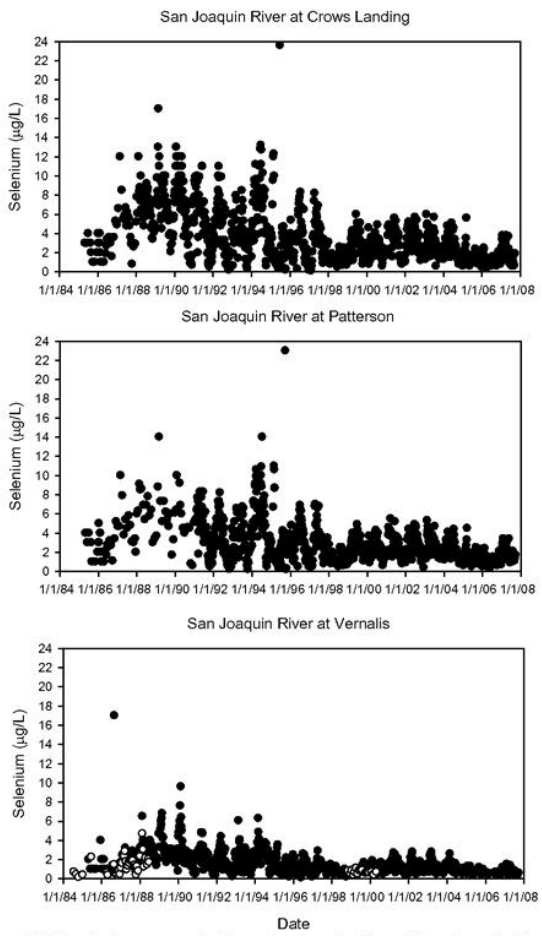


**Figure 3-17** **Total selenium concentrations along main stem of San Joaquin River at Crows Landing (below grassland bypass project), at Patterson, and at Vernalis (Data Source: Central Valley RWQCB)**



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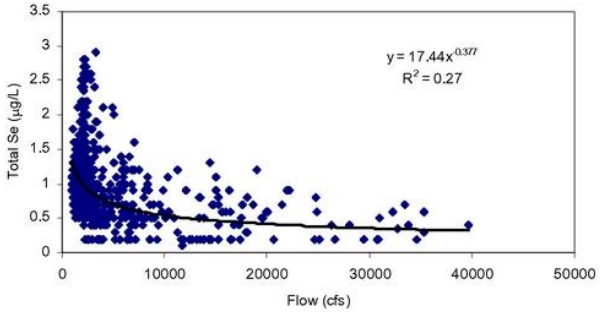


**Figure 3-18** **Relationship between total selenium and flow at San Joaquin River at Vernalis (Data source: Central Valley Regional Water Quality Control Board SWAMP study and USGS).**

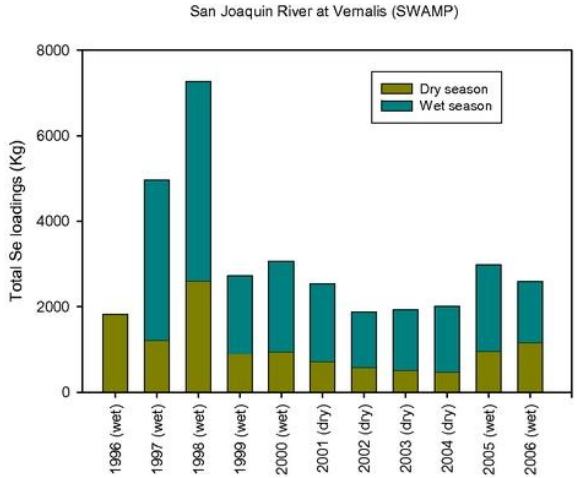


**Figure 3-19** **Dry and wet season total selenium loadings at San Joaquin River at Vernalis, estimated from concentrations from SWAMP study.**



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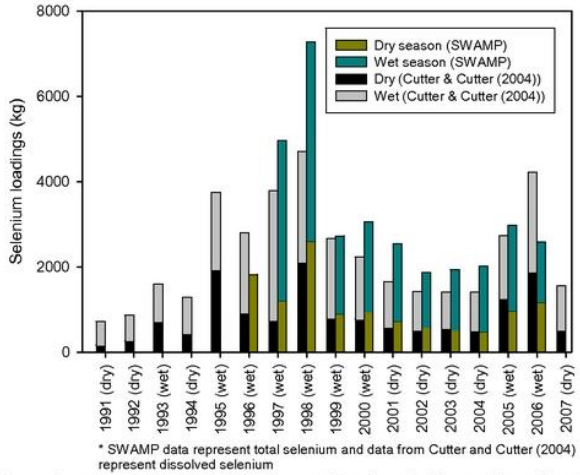


**Figure 3-20** **Comparison of selenium loadings at San Joaquin River at Vernalis estimated from Cutter and Cutter (2004) data and data from SWAMP study.**

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.



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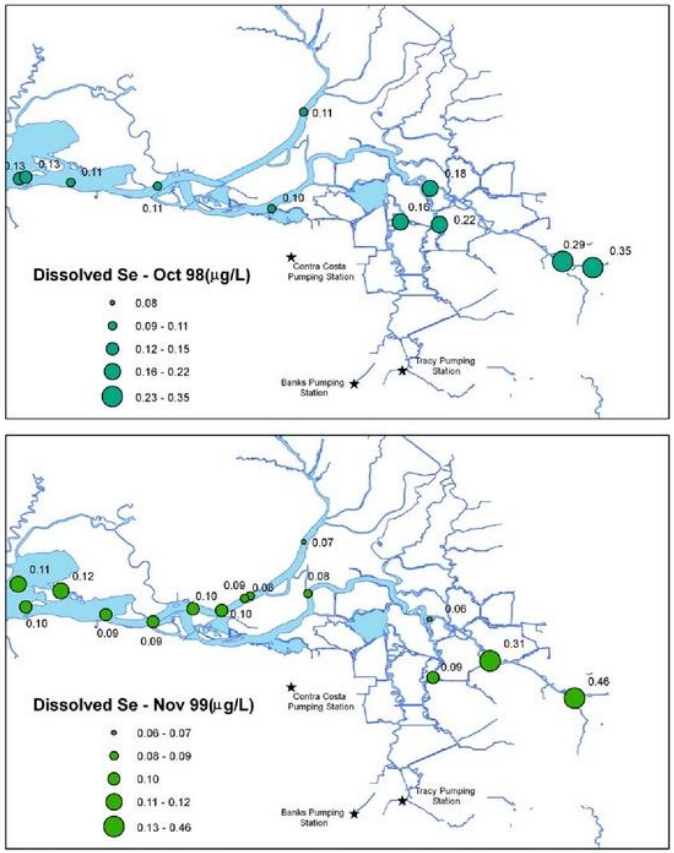


**Figure 3-21** **Dissolved selenium concentrations at various locations of the Delta and North Bay in October 1998 (NDOI = $4.27 \times 10^{10}$ L/d) and November 1999 (NDOI = $1.07 \times 10^{10}$ L/d) sampling (Cutter and Cutter, 2004).**

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.



## *No comments*

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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.

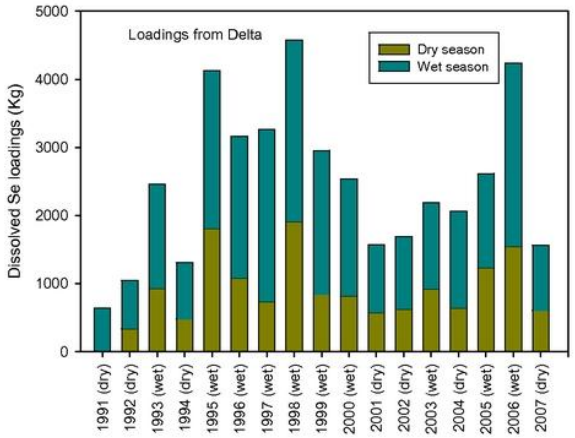


**Figure 3-22** **Estimated selenium loadings from the Delta to the bay as a result of inputs from Sacramento River at Freeport and San Joaquin River at Vernalis, assuming a "Delta Removal Constant" of 0.60.**

Both Methods 1 and 2 have limitations in estimating selenium loads from the Delta. The previous method based on RMP monitoring dataset 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.



## *No comments*

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### 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 ± 0.90 × 109 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.

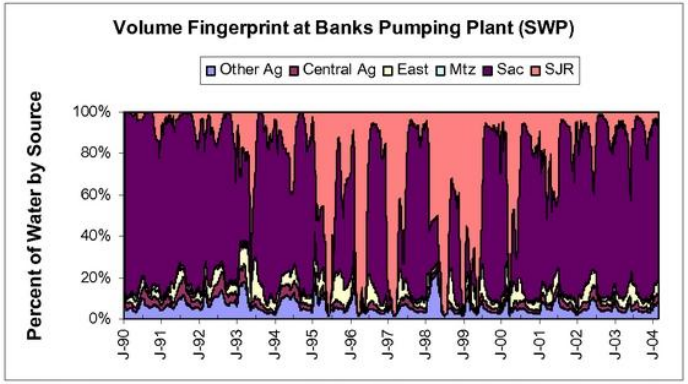


**Figure 3-23** **Long-term percentage contribution of flows at the Banks Pumping Plant (data provided by DWR; Tetra Tech, 2006).**



## No comments

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Concentrations at pumping plants were estimated as:

$$Cexp = (Qsac * Csac + Qsjr * Csjr) / Qexp \quad (1)$$

Where Cexp is daily concentration in the aqueduct, Qsac is export flow originating from the Sacramento River, Csac is daily selenium concentration at the Sacramento River at Freeport (estimated from monthly concentrations from Cutter and Cutter, 2004), Qsjr is export flow originating from the San Joaquin River, Csjr 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 Qexp 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.



## No comments

- n/a -

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://wwwomwq.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



## No comments

- n/a -

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 µg/g (n =5) at the Sacramento River and 0.66 ± 0.42 µg/g (n =5) at the San Joaquin River (Doblin et al. 2006). Therefore an average concentration of 0.64 µg/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).



## No comments

- n/a -

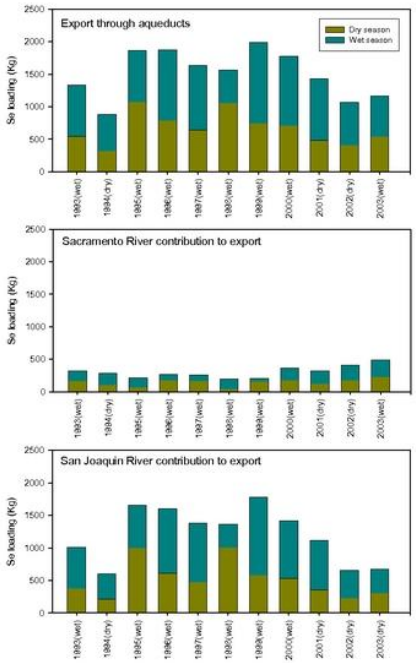


**Figure 3-24** **Estimated selenium loadings through the aqueducts and contributions from the Sacramento River and the San Joaquin River.**

## *No comments*

- n/a -

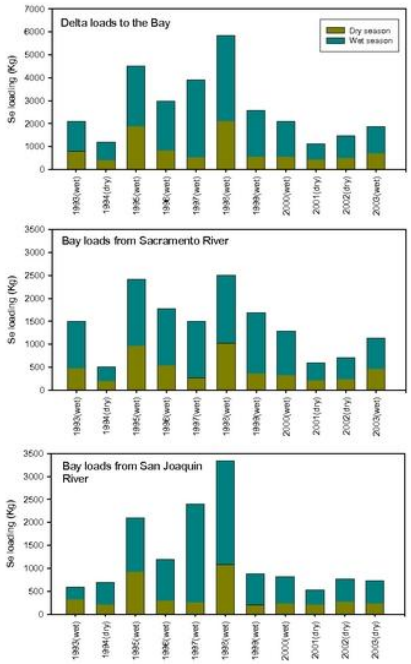


**Figure 3-25** **Estimated selenium loadings from the Delta to the Bay as the difference between loads from the Rivers and export through aqueducts, as well as contributions attributed to the Sacramento River and the San Joaquin Rivers individually.**

## *No comments*

- n/a -

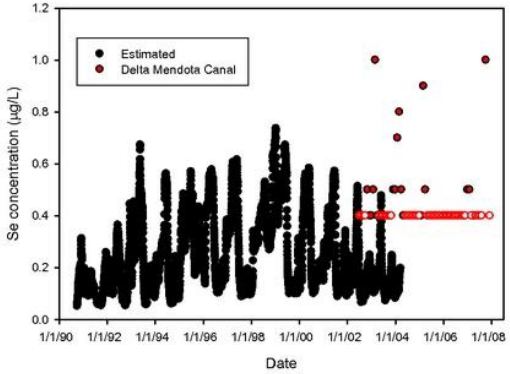


**Figure 3-26** **Estimated selenium concentrations in the aqueducts using flow weighted method compared to observed concentrations in Delta Mendota Canal near Tracy Headworks (MP 3.50) (Open circles indicates values below detection limit of 0.4 µg/L).**

### 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 dissolves 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.



## *No comments*

- n/a -

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).



## No comments

- n/a -

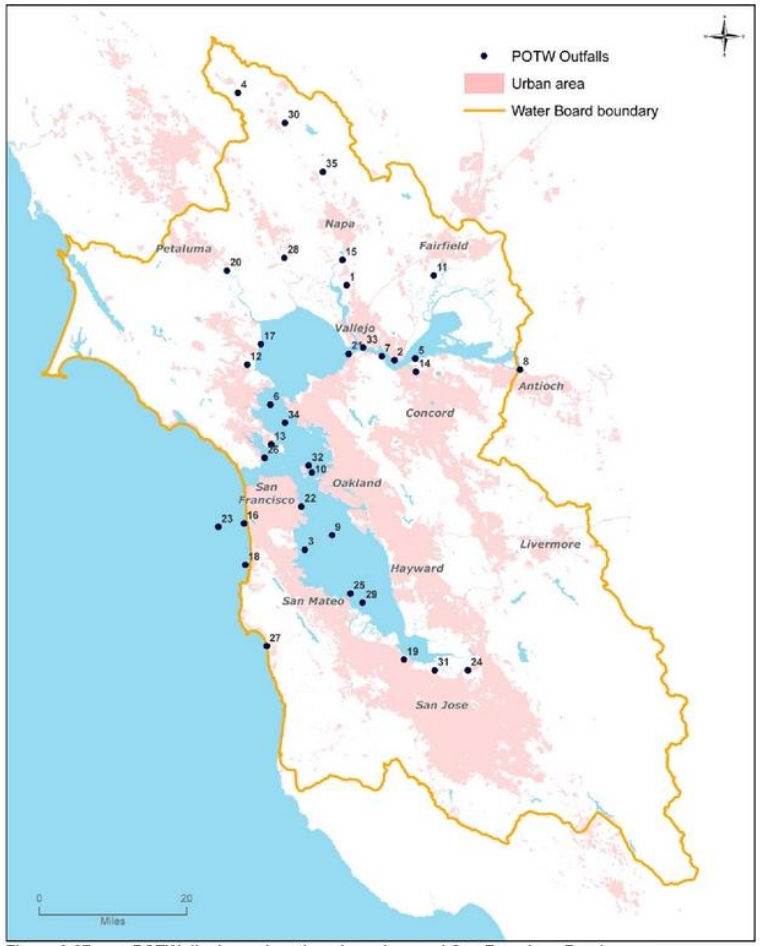


**Figure 3-27** **POTW discharge locations in and around San Francisco Bay (source: SFBRWQCB, Basin Plan).**



## *No comments*

- n/a -

**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)<br>(Novato Wet) | 17 | 0.475<br>0.833 | 0.05<br>0.32 | 0.4<br>0.4 | 0.5<br>1 | 4<br>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



## *No comments*

- n/a -

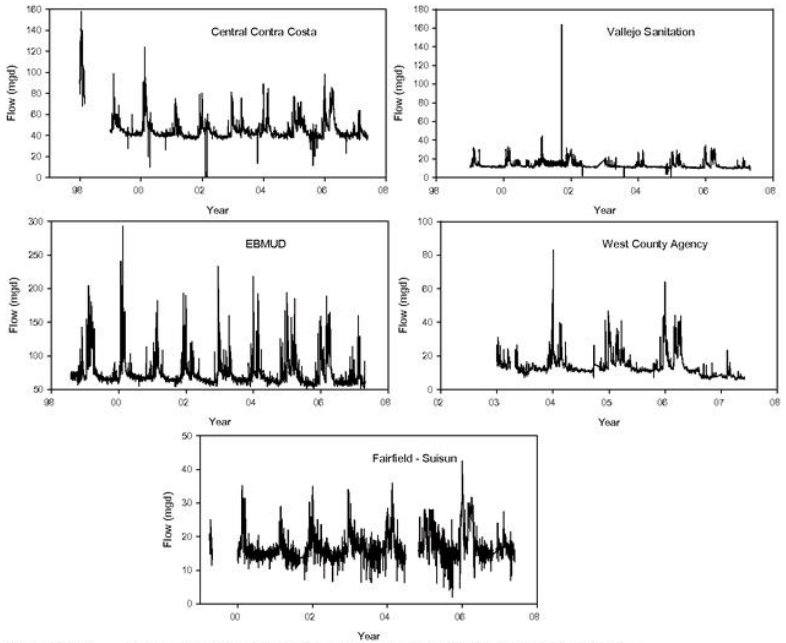


**Figure 3-28** **Daily effluent average flow at five largest dischargers in North Bay.**



## *No comments*

- n/a -

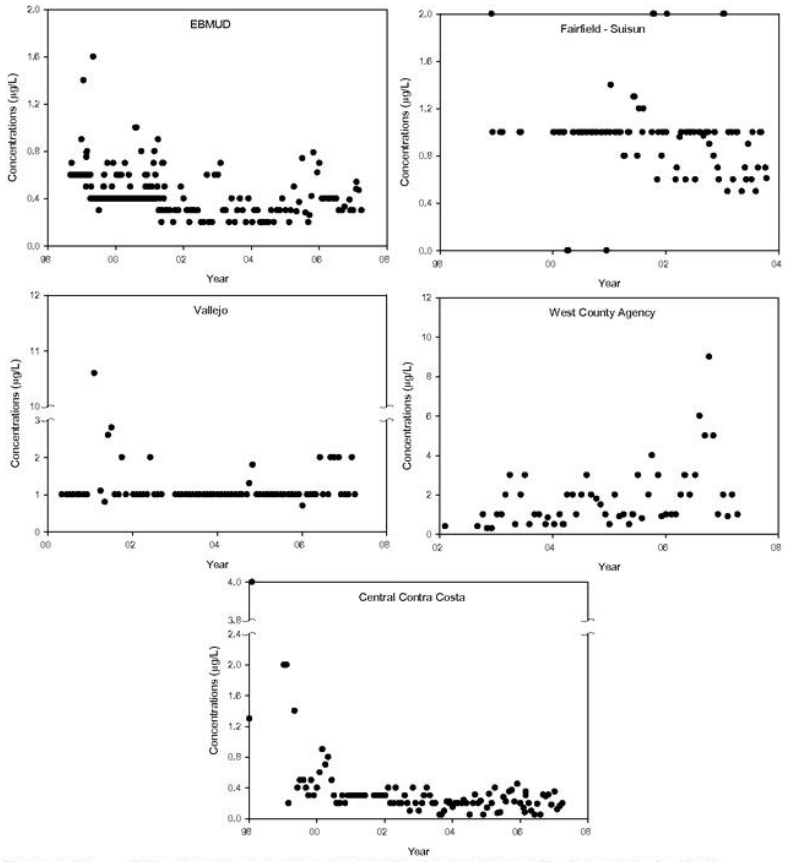


**Figure 3-29** **Effluent maximum concentrations for the five largest dischargers in the North Bay.**

## *No comments*

- n/a -

**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)<br>(E-003 S) | 1 | 0.89<br>0.99 | 1.42<br>1.46 | 1.53<br>1.43 |
| City of Benicia | 2 | 3.0 | 3.5 | 3.4 |
| City of Calistoga[3] (E-001 dry)<br>(E-002 wet) | 4 | 0.87<br>0.65 | 0.60<br>0.46 | 0.20 |
| 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)<br>(E-004) | 11 | 17.0<br>1.44 | 17.5<br>1.48 | 16.8<br>1.68 |
| Las Gallinas Valley S.D. (E-001)<br>(E-002) | 12 | 3.75<br>1.44 | 2.48<br>0.95 | 4.0 |
| 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)<br>(Wet weather) | 15 | 3.8<br>13.98 | 1.49<br>2.60 | 2.94<br>10.34 |
| Novato S.D. E-001 Ignacio Dry<br>E-002 Novato Wet | 17 | 4.01<br>2.23 | 2.63<br>2.57 | 2.90<br>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)<br>(Mare deep) | 33 | 13.2<br>2.69 | 17.5<br>2.85 | 15.66<br>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.



## *No comments*

- n/a -

**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 |

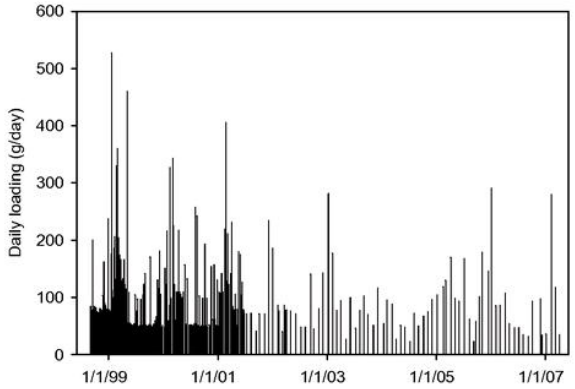


**Figure 3-30 Estimated daily total selenium loadings from EBMUD.**

### 3.6. PETROLEUM REFINERIES

Mean selenium concentrations at the refineries range between 11.9 – 27.7 µg/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 µg/L. No relationship between concentrations and flow were observed. The annual loadings were calculated by summing the daily loadings. The



## *No comments*

- n/a -

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



## No comments

- n/a -

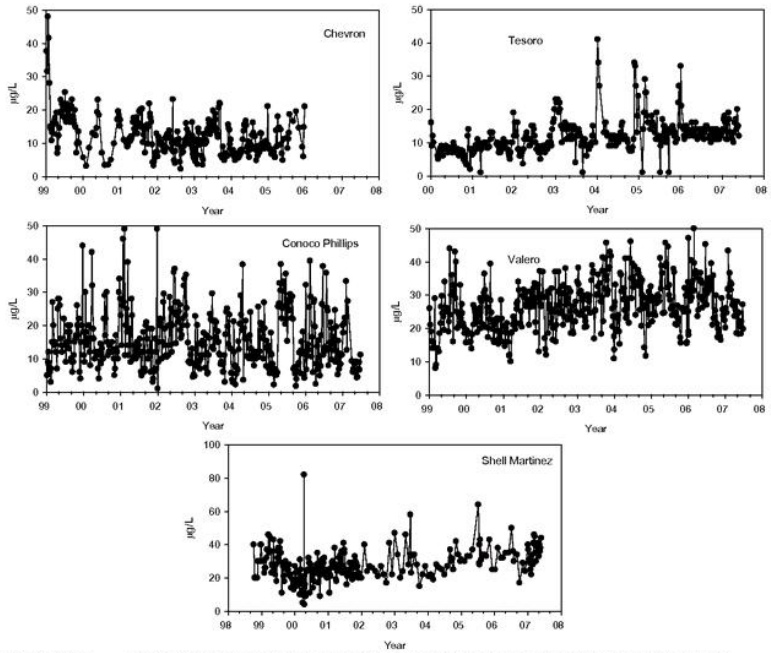


**Figure 3-31** **Effluent daily maximum selenium concentrations for the refineries in the North Bay.**



## *No comments*

- n/a -

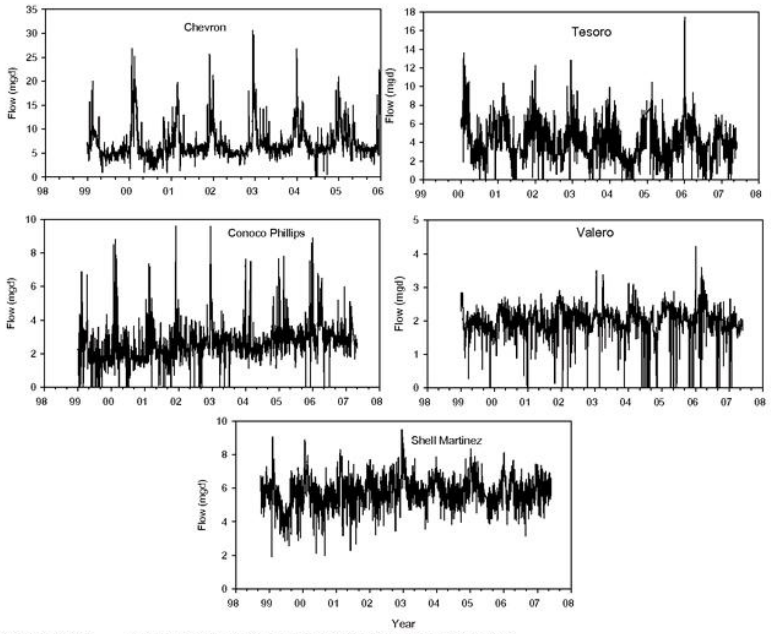


**Figure 3-32** **Daily average effluent flow rate from the refineries.**

## *No comments*

- n/a -

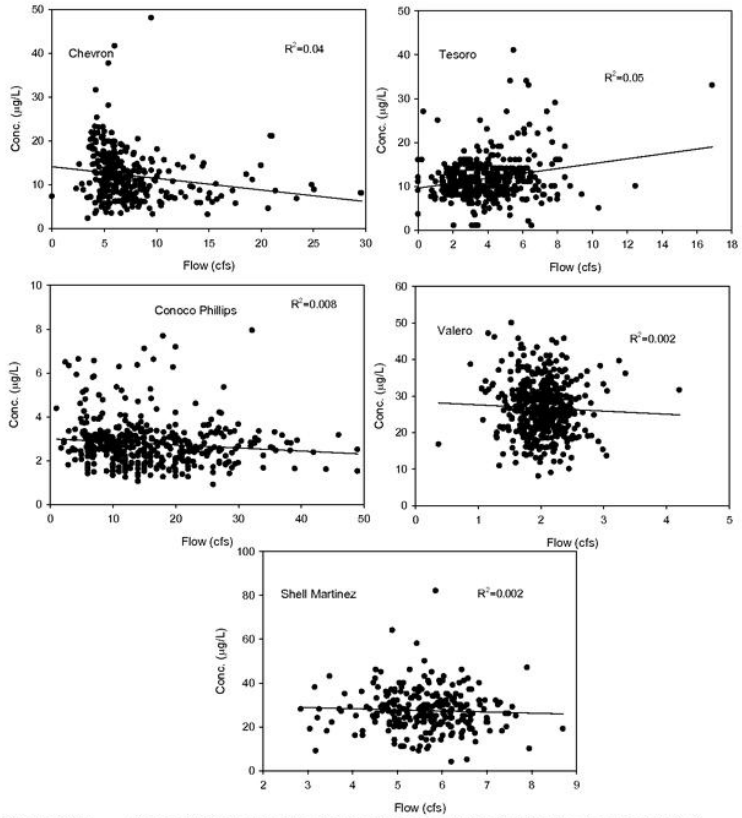


**Figure 3-33** **Concentrations and flow for the refineries in the North Bay. No meaningful correlations were found; the regression lines in the plots are to illustrate the lack of a relationship between flows and concentrations.**



## *No comments*

- n/a -

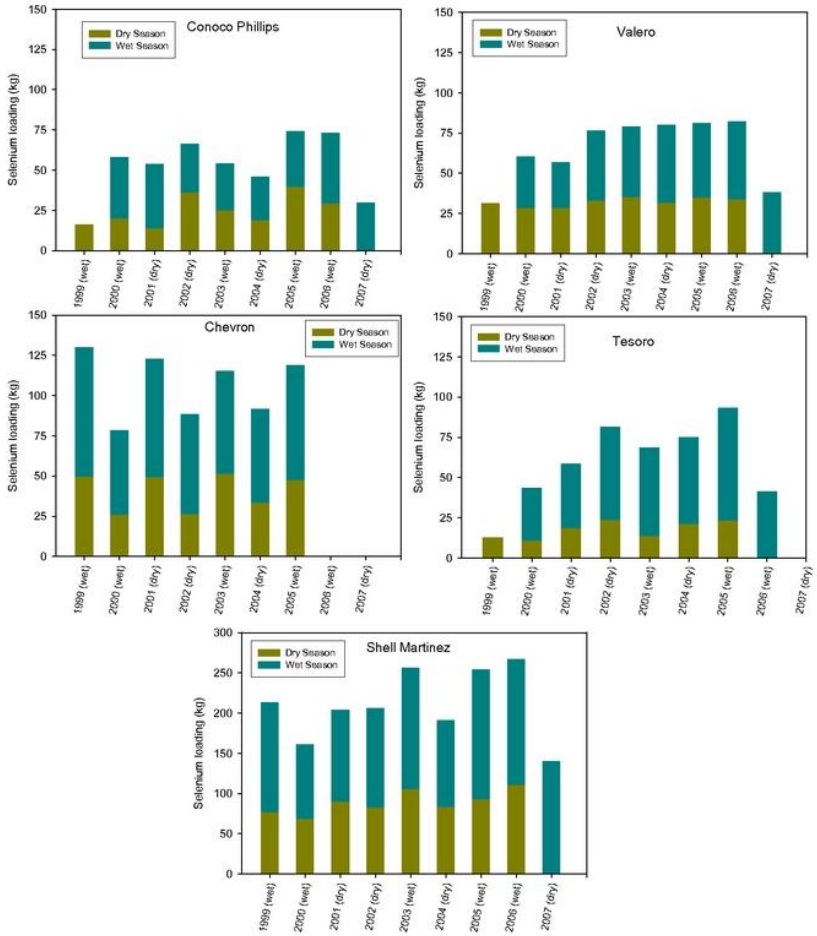


**Figure 3-34** **Dry and wet season selenium loadings from refineries for the years of 1999-2007.**



## *No comments*

- n/a -

### 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 ($1.4 \times 10^{11}$ kg; Davis (2003), cited in Abu-Saba and Ogle, 2005) and mean selenium concentrations of 0.25µg/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 $cm/m^2$/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 µg/g. Sediment loss of Suisun and San Pablo Bay is estimated to be around 1,100 M kg/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).



## No comments

- n/a -

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 |

[1]Source 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 two 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 $Mm^3$/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.



## No comments

- n/a -

### 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.



## *No comments*

- n/a -

**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 |

[1]Based on TSS loadings by Davis et al. (2000), times selenium content in particulate material of Sacramento River

[2]Based on TSS loadings by McKee et al. (2006) and mean selenium content in particulate material of Sacramento and San Joaquin Rivers

[3]Based on average Delta outflow of 25000 $Mm^3$. Outflow only includes loads contributed by the northern reach.

[4]Sediment diffusion rate estimated by Meseck (2002).

[5]Based 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.



## *No comments*

- n/a -

**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.



## *No comments*

- n/a -

**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 |

[1]From 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.



## No comments

- n/a -

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 (Meseck, 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).



## No comments

- n/a -

## 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.



***No comments***

- n/a -

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



## *No comments*

- n/a -

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.



## No comments

- n/a -

## *No comments*

- n/a -

## 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 µg/g, with a few exceptions. These concentrations correlate 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 into 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



***No comments***

- n/a -

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.



## No comments

- n/a -

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## *No comments*

- n/a -

## 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.



## *No comments*

- n/a -

(3) Cs = Kd*Cw, where Cs: concentration in particulate, Kd: partition coefficient, Cw: dissolved concentration. Cw 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 |



## *No comments*

- n/a -

**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 |



## *No comments*

- n/a -

**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 (µg/g) | Mean (µg/g) | Standard Deviation (µg/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 |



## *No comments*

- n/a -

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 occured 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 | | |



***No comments***

- n/a -

| 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 |



***No comments***

- n/a -

| 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 (Tiburon) | 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 |



## *No comments*

- n/a -

Estuaries and Coasts
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# Modeling Fate, Transport, and Biological Uptake of Selenium in North San Francisco Bay

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**Abstract** Selenium behavior in North San Francisco Bay, the largest estuary on the US Pacific coast, is simulated using a numerical model. This work builds upon a previously published application for simulating selenium in the bay and considers point and non-point sources, transport and mixing of selenium, transformations between different species of selenium, and biological uptake by phytoplankton, bivalves, and higher organisms. An evaluation of the calibrated model suggests that it is able to represent salinity, suspended material, and chlorophyll *a* under different flow conditions beyond the calibration period, through comparison against long-term data, and the distribution of different species of dissolved and particulate selenium. Model-calculated selenium concentrations in bivalves compared well to a long-term dataset, capturing the annual and seasonal variations over a 15-year period. In particular, the observed lower bivalve concentrations in the wet flow periods, corresponding to lower average particulate selenium concentrations in the bay, are well represented by the model, demonstrating the role of loading and hydrology in affecting clam concentrations. Simulated selenium concentrations in higher organisms including white sturgeon and greater scaup also compared well to the observed data in the bay. Finally, a simulation of changing riverine inflows into the bay that might occur as a consequence of proposed hydrologic modifications indicated significant increases in dissolved and particulate selenium concentrations in the bay. The modeling framework allows an examination of the relationship between selenium loads, variations in inflow, in-bay concentrations, and biota concentrations to support management for limiting wildlife impacts.

**Keywords** Bioaccumulation · Selenium speciation · TMDL · Estuarine modeling · ECoS

## Introduction

Selenium is a limiting nutrient to aquatic organisms at low concentrations; however, it becomes toxic when concentrations are elevated (Harrison et al. 1988; Lauchli 1993; Lemly 1996). The element is toxic to fish and birds due to its adverse impacts on the reproductive system (Lemly 1985; Presser and Luoma 2006). Selenium can substitute for sulfur in the structure of proteins and therefore causes deformities in embryos or inhibition of the hatchability of eggs (Skorupa 1998). Under the Clean Water Act of the USA, North San Francisco Bay (NSFB) is listed as being impaired for selenium, due to high concentrations observed in fish tissues (particularly in white sturgeon, *Acipenser transmontanus*, up to 50 μg/g dry weight) and diving ducks (such as greater scaup, *Aythya marila* up to 35 μg/g dry weight in muscle tissues) (White et al. 1988, 1989; Urquhart et al. 1991; SFEI 2006). NSFB is an important water body for the study of selenium biogeochemistry and ecotoxicology, because it is the largest estuary on the Pacific coast of

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***No comments***

- n/a -

the USA and receives significant selenium loadings from sources that are directly related to human activity: it is downstream of irrigated selenium-bearing soils of the semi-arid San Joaquin Valley (representing 7 % of total US agricultural production and four of the top five agriculturally productive counties in the US), and it receives selenium discharged from five major oil refineries (which together constitute 5.6 % of the total refining capacity of the USA; based on data from the US Census of Agriculture 2007; California Energy Commission 2012). Selenium has been a contaminant of interest in this region since the discovery of deformed waterfowl in the Kesterson Wildlife Refuge in San Joaquin Valley, which received most of its water from agricultural drainage (Ohlendorf et al. 1988).

Selenium is present in the aquatic environment in several different forms (Cutter 1992). Dissolved forms of selenium include inorganic selenite ($SeO_3^{2-}$+$HSeO_3^-$), selenate ($SeO_4^{2-}$), and organic selenides. The particulate forms include elemental selenium, organic selenides, and selenite and selenate adsorbed on particles. Selenium in biogenic particles is principally composed of organic selenide (Cutter and Bruland 1984) with each species being subject to different transformations and biological uptake (Suzuki et al. 1979; Measures et al. 1980; Cutter and Bruland 1984). Particulate organic selenides can decompose and release dissolved organic selenides at relatively fast rates (>0.2/day, Cutter 1982). Organic selenides can be oxidized to selenite and further to selenate and this has been described using pseudo-first-order reactions (Cutter and Bruland 1984). The oxidation of organic selenides to selenite can occur on the order of days, while oxidation from selenite to selenate can take years (Cutter 1992; Meseck and Cutter 2006).

Dissolved forms of selenium can be taken up by phytoplankton and bacterioplankton communities. The uptake of dissolved selenium by these organisms is a key step in selenium entering the food web (Luoma et al. 1992; Wang et al. 1996). The bioavailability of dissolved selenium differs by chemical form, with selenite and organic selenides being taken up more rapidly than selenate (Riedel et al. 1996). Despite low selenium concentrations in the water column, certain species of phytoplankton can concentrate selenium to relatively high concentrations (Baines and Fisher 2001; Doblin et al. 2006). Organic selenides in cells can be released into the environment through excretion, cell lysis, or grazing (Cutter 1982).

The uptake of selenium by invertebrates is mainly through the ingestion of particulates (Luoma et al. 1992; Sanders and Gilmour 1994; Wang and Fisher 1996), especially particulate organic selenides which are more easily assimilated by invertebrates. Measured assimilation efficiencies for elemental selenium range from 2 to 28 % (Schlekat et al. 2000), while assimilation efficiencies for organic selenium range from 53 to 89 % (Schlekat et al. 2002). As with phytoplankton, the accumulation of particulate selenium in invertebrates and zooplankton differs by species. Certain species of invertebrates (e.g., the clam *Corbula amurensis* that is abundant in NSFB) are able to accumulate selenium to relatively high concentrations due to high food ingestion rates and slow excretion (Stewart et al. 2004), resulting in relatively high selenium concentrations in the benthic food web.

Sources of selenium to the NSFB include riverine inputs from the Sacramento and San Joaquin Rivers, tributaries surrounding the NSFB, discharge from refineries, and municipal and industrial wastewater treatment plant discharges. The NSFB water column is characterized by low selenium concentrations (~0.2 μg/L); however, bioaccumulation by *C. amurensis*, may be a pathway leading to high selenium in certain benthic-feeding fish and birds.

The San Francisco Bay Regional Water Quality Control Board is in the process of developing a selenium total maximum daily load (TMDL) for NSFB to address this impairment. Under the Clean Water Act, a TMDL is required when a water body is listed as impaired due to one or more contaminants and sets in motion a process to manage and control the impairment. To effectively address impairment, TMDLs need tools, often in the form of numerical models, to represent the linkage between sources of contamination and biological endpoints, including concentrations in the tissues of target organisms. The objective of the present study is to develop a model representing the transport, fate, and uptake of selenium in the benthic food web of NSFB, focusing on phytoplankton, clams, and fish and bird species that consume these clams. The model is calibrated using the best available data on hydrology, selenium loading from the major rivers, petroleum refineries, municipal wastewater treatment plants, and other industrial sources and selenium speciation in different compartments as reported in monitoring programs and the scientific literature over the last two decades.

The modeling framework builds on a previous study of selenium biogeochemistry in NSFB (Meseck and Cutter 2006), developed using an estuary modeling framework (ECoS3) (Harris and Gorley 1998). The previous study was modified for the TMDL by: (1) using more recent selenium loads from five major refineries and principal riverine sources, Sacramento and San Joaquin Rivers, (2) adding selenium loads from smaller, local tributaries, and all municipal and industrial dischargers with discharge permits; (3) modification of the model to consider particulate selenium, total suspended material (TSM), and phytoplankton inputs from the San Joaquin River; (4) changing the riverine boundary conditions of TSM, chlorophyll *a* and different species of particulate selenium to time-varying inputs; and (5) expanding the model to simulate



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selenium concentrations in biota (clams, fish, and diving ducks). The final change is especially important because the impairment in NSFB is driven by concentrations in biota. The above changes necessitated a recalibration and extension of the Meseck and Cutter (2006) model, as detailed in the following section while retaining the basic setup of the original work. The updated model was recalibrated for the 1999–2000 water years, and then used to simulate long-term selenium dynamics in NSFB for the period of 1999–2008. Through this development and integration process, the key research questions to be answered are: can we describe the speciation of selenium in the waters of NSFB under different flow and loading conditions, the changing seasonal and long-term concentrations of selenium in the clam *C. amurensis*, monitored at a regular frequency as a sentinel species in the bay over 1995–2010, and concentration patterns in other predator species that consume *C. amurensis*? A reasonable representation of these observations lends credibility to the use of this modeling framework for management of selenium in NSFB over the coming years during which many changes are possible, including changes in land use, upstream water diversions, sea level rise, and modified freshwater outflows. More generally, the framework for integration of data and mechanistic processes presented here may be applicable to the management of selenium in estuaries receiving inflows from urbanized and developed watersheds, although affected species and food webs may differ.

## Methods

### ECoS Modeling Framework

ECoS3 is a modeling framework developed by the Center for Coastal and Marine Sciences (Plymouth Marine Laboratory, UK) that can be used to simulate transport and dynamics of dissolved and particulate constituents in a one-dimensional (1-D) or 2-D form for an estuary (Harris and Gorley 1998, 2003). By using a single box or a multiple box approach, the model will simulate salinity, nutrients, TSM, and biological productivity once the shape, geometry, and tidal movement in the estuary are established (Harris and Gorley 1998). ECoS3 considers transport due to advection and dispersion, transformations between species through exchange or reactions, and changes through point or non-point inputs and outputs. ECoS3 has been widely applied to simulate different constituents (e.g., salinity, suspended particles, carbon, nitrogen, nutrients, Zn, and Ni) in estuaries including the Humber Estuary in UK (Harris 2003; Tappin et al. 2003), Tweed Estuary (Punt et al. 2003; Uncles et al. 2003), and Tamar Estuary (Liu et al. 1998). Meseck and Cutter (2006) used ECoS3 to focus on simulating transport and biogeochemistry of selenium in 1-D form in the NSFB.

### Model Domain and Components

As in Meseck and Cutter (2006), the model was applied starting from the Sacramento River at Rio Vista, extending through NSFB to the Golden Gate Bridge (Fig. 1), with Rio Vista constituting the freshwater boundary, and the Golden Gate Bridge the ocean boundary. The model consists of 33 linked cells, each 3 km wide, representing this domain, with external flows and selenium load inputs at various intermediate locations (Fig. 2). The Sacramento-San Joaquin Delta is not explicitly modeled in this work: Sacramento River flows at Rio Vista are the main freshwater input, with inflows from San Joaquin River added at the confluence 19 km from Rio Vista. Flows at Rio Vista are measured, with the contribution from San Joaquin River estimated as the difference between the Delta outflow and the Rio Vista flow. Tributary flows from 10 local watersheds surrounding NSFB, 5 major refineries, and 23 additional municipal wastewater and industrial point sources were added to the model corresponding to their distance from the head of the estuary at Rio Vista. These sources are identified and their distances from Rio Vista listed in Table 1 in the Electronic supplementary material (ESM).

Meseck and Cutter (2006) used the model to simulated salinity, TSM, phytoplankton, and different species of dissolved and particulate selenium (dissolved selenate, selenite, organic selenide, particulate elemental selenium, particulate organic selenides, and adsorbed selenite and selenate). The modified and recalibrated model presented here simulates these constituents and selenium concentrations in bivalves and higher trophic level organisms (white sturgeon and greater scaup).

As a first step, salinity in the bay is simulated because it represents the advection and dispersion of all dissolved water column constituents in the estuary (Harris and Gorley 1998). Accurate simulation of salinity is an indicator that the advection and dispersion of dissolved species is represented adequately. The simulation of TSM indicates how well the fate and transport of all other constituents associated with particulates in the estuary is simulated. TSM concentrations also affect reactions of selenium with particulates and the distribution of particulate selenium in the estuary. Simulation of phytoplankton greatly affects the fate of selenium, because selenium uptake by phytoplankton is an important first step in subsequent foodweb uptake (Luoma et al. 1992). Loads, transport, and transformations of different species of selenium are important modeling components as bioavailability differs among the different species of selenium. The bioaccumulation of selenium through the foodweb is an important component of this model as it links selenium



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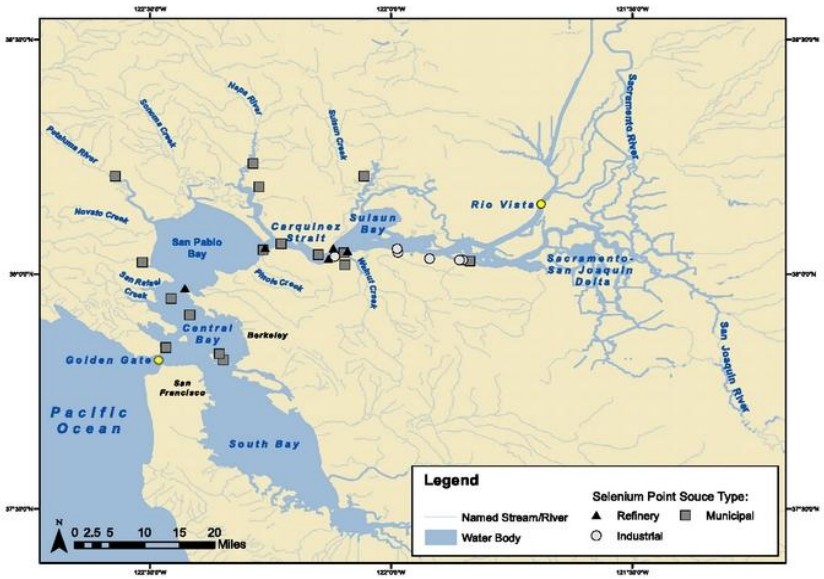


**Fig. 1** San Francisco Bay region and surroundings. The model uses Rio Vista on Sacramento River as the starting point of the simulations and spans the region to Golden Gate, following Meseck and Cutter (2006). San Joaquin River inflows are added as a tributary 19 km downstream of Rio Vista. Other tributaries and point sources are also shown and listed in Table 1 in the ESM. The Delta is not explicitly modeled in this application

concentrations in the water column to biota of ecological concern.

To adapt the Meseck and Cutter (2006) model for the present application required some modifications to the loads and model formulation, as outlined here. Refinery loads were updated using daily selenium inputs from five refineries in the NSFB, estimated based on daily flow and weekly concentrations for the period of 1999–2007. These loads were added to model cells based on their discharge locations. In addition, selenium loads from local tributaries to NSFB (i.e., in addition to the major riverine flows through the Delta) were added to the model based on their discharge locations. These loads were not identified in the prior application and may be significant during wet months. Loads from publicly owned treatment works and other point source dischargers in the NSFB were added to the model based on their discharge locations. All sources of selenium are identified in Fig. 1. 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. In simulating the TSM, phytoplankton, and particulate selenium, the current model uses observed concentrations as much as possible in defining the riverine boundary conditions.

The transfer of dissolved selenium to particulate selenium through phytoplankton uptake is an important process in its bioaccumulation. Therefore, particulate selenium associated with phytoplankton uptake within the estuary was tracked as a separate constituent and was added to the total particulate selenium. At the boundaries, the input of phytoplankton and all other forms of particulate selenium were estimated separately through calibration. Simulated Se/C ratio in phytoplankton was also tracked by the model and was compared with data observed for species found in the bay. Finally, a dynamic multi-pathway bioaccumulation model



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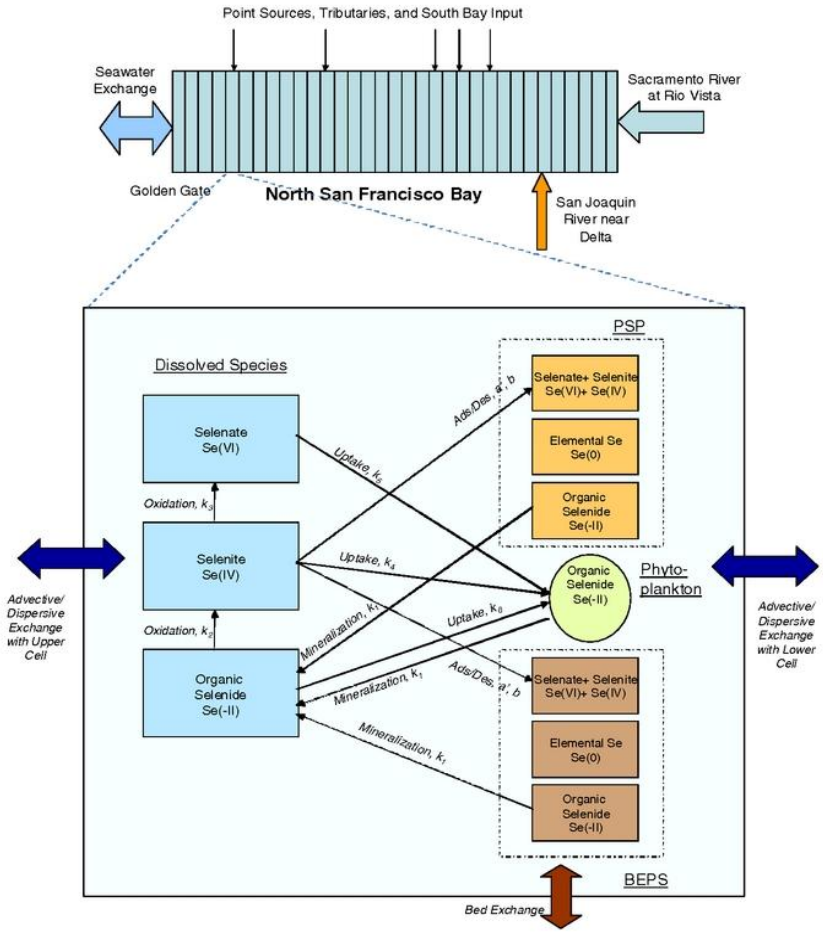


**Fig. 2** Schematic of model representation of the NSFB, showing model cells or nodes (*vertical boxes*), boundary conditions, and external loads. Each cell is 3 km wide. The locations of the external loads are illustrative and are added in the model location at the approximate location they enter the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

(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)



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**Table 1** DYMBAM model parameters for *Corbula amurensis*

| $K_u$ (L $g^{-1}$ $day^{-1}$) | IR (g $g^{-1}$ $day^{-1}$) | AE (%) | $K_e$ ($day^{-1}$) | Growth rate (per day) | Tissue Se concentration (mg/kg) | References |
|---|---|---|---|---|---|---|
| 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) |

*DYMBAM* dynamic multi-pathway bioaccumulation model, *AE* assimilation efficiencies

were used to predict bioaccumulation of selenium to the higher trophic levels (bivalves, benthic-feeding fish, and diving ducks).

The above changes entailed a recalibration of the model and evaluation against the most recently available data in NSFB including salinity, TSM, chlorophyll *a*, dissolved and particulate selenium, and selenium concentrations in clams for the period beyond 1999 (US Geological Survey (USGS) monthly cruises in the bay; SFEI 2006; Doblin et al. 2006; Kleckner et al. 2010). The complete modeling framework development, calibration, and application to NSFB are detailed in a report prepared for the TMDL effort (Tetra Tech 2010; available on the Internet at: http://www.swrcb.ca.gov/rwqcb2//water_issues/programs/TMDLs/seleniumtmdl.shtml).

## Selenium Transformations Simulated

While in the water column, different species of selenium can undergo biological and chemical transformations, and these transformations were simulated by the model (Cutter 1982; Cutter 1992). Transformations of dissolved selenite simulated by the model 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. Particulate organic selenides can undergo mineralization to form dissolved organic selenide (Cutter 1982). The exchange of selenium between different compartments simulated by the model is shown schematically in Fig. 2, identifying the different dissolved and particulate species, and the exchanges between them. In this formulation, particulates are tracked as three phases, permanently suspended particulates (PSP), composed of fine material that remains in suspension, bed exchangeable particles (BEPS), composed of larger particles that originate from sediment resuspension, and phytoplankton. The transformations among different species of dissolved and particulate selenium are modeled as a set of first-order reactions, labeled with rate constants from $k_1$ to $k_6$, an approach similar to that by Meseck and Cutter (2006). Under oxic conditions, such as those occurring in the waters of the NSFB, the key transformations include oxidation of organic selenide to selenite, and further oxidation of selenite to selenate, as well as uptake of all dissolved species by particulate phases (PSP, BEPS, and phytoplankton). Values of the rate constants were estimated from the literature and are listed in Table 2 in the ESM. These ranges were used as a starting point for the modeling, and where the range was broad, the parameters were adjusted to obtain a best fit to the data from the NSFB. In the work, the rate constants $k_1$ and $k_2$ were estimated through calibration, whereas $k_3$ through $k_6$ were based on literature estimates. In general, these rate constants indicate that the oxidation of organic selenide is relatively rapid, although oxidation of selenite to selenate is a very slow process. Also, uptake of selenide and selenite onto particulate phases was more rapid than for selenate.

## Selenium Bioaccumulation Through the Foodweb

### *Selenium Uptake by Bacteria and Phytoplankton*

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

### *Selenium Bioaccumulation Through Bivalves*

Bioaccumulation of particulate selenium to lower trophic level organisms (e.g., bivalves) is simulated using a 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.

The dynamic form of the DYMBAM model is as follows:

$$\frac{dC_{mss}}{dt} = k_u \times C_w + AE \times IR \times C_f - k_e \times C_{mss} \quad (1)$$

where $C_{mss}$ is selenium concentration in tissue (in micrograms per gram), $k_u$ is the dissolved metal uptake rate



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constant (in liters per gram per day), $C_w$ is the dissolved metal concentrations in water (in micrograms per liter), AE is the assimilation efficiency (in percent), IR is the ingestion rate (in grams per gram per day), $C_f$ is the metal concentration in food (e.g., phytoplankton, suspended particulate matter, and sediment; in micrograms per gram), and $k_e$ is the efflux rate (in $day^{-1}$). Uptake through the waterborne pathway was found to be negligible (Luoma et al. 1992) and not considered. Parameter values in Eq (1) for uptake of selenium by *C. amurensis* are derived from Stewart et al. (2004) and shown in Table 1. Parameters for different metals and different species of organisms have been quantified in previous studies (summarized in Luoma and Rainbow 2005). The filter-feeding organism *C. amurensis* was found to have a higher assimilation efficiency and lower elimination rate, and thus accumulating selenium to higher concentrations than other bivalve species common in the bay, such as *Corbicula fluminea* (Lee et al. 2006; Linville et al. 2002). Bioaccumulation into bivalves considers different efficiencies of absorption for different selenium species (Table 2). Assimilation efficiencies (AE) measured by Schlekat et al. (2002) for organic selenide are in a relatively narrow range for different species of algae and are generally high (53–89 %). AE for elemental selenium are generally low (2–28 %), with biogenic particulate elemental selenium showing higher AE. In developing model predictions in this work, 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 (Fig. 3).

A range of ingestion rates has also been estimated for *C. amurensis* by Lee et al. (2006) and covers a wide range from 0.1 to 1.0 $g g^{-1}$ $day^{-1}$ (Table 1). The ranges in assimilation efficiency and ingestion rates were used to forecast the range of selenium concentrations in bivalves. The predicted selenium concentrations in bivalves were compared with observed data by Stewart et al. (2004). In forecasting the long-term selenium concentrations in bivalves, an ingestion rate of 0.65 $g g^{-1}$ $day^{-1}$ (roughly the midpoint value) was used in model predictions.

### *Selenium Bioaccumulation to Higher Trophic Levels (Fish and Diving Ducks)*

A ratio between selenium concentrations in the tissues and diet of organisms, the trophic transfer factor (TTF) can be used in estimating bioaccumulation of selenium through the food web, once dietary concentrations are known (Presser and Luoma 2010). The ratio can be derived based on kinetic uptake rates or observed concentrations of diet and tissue. For example, the TTF for invertebrates can be derived as: TTF=(AE)(IR)/$k_e$, where AE is the assimilation efficiency; IR is the ingestion rate, and $k_e$ is the elimination rate. The TTFs are a relatively simple and effective way to incorporate the complex processes of biological uptake from bivalves (e.g., clams) to predator species (e.g., sturgeon and scaup) in this model. The significance of clams in the diet of these species has been reported previously (Stewart et al. 2004). TTFs for fish have been found to vary over a relatively narrow range across species and habitats, based on an examination of data from 29 field studies (Presser and Luoma 2010). For several fish species studied the TTFs for selenium range from 0.52 to 1.6 (Presser and Luoma 2010), and a value of 1.3 was reported for white sturgeon. A TTF of 1.8 has been reported for bird egg concentrations in mallards (Presser and Luoma 2010).

**Table 2** Literature values of assimilation efficiencies (AE) for different selenium species for *Corbula amurensis*

| Species | AE | Origin | References |
|---|---|---|---|
| Se(0)[a] | 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) |
| *Cryptomonas* sp. | 88.9 % | Algae cells | Schlekat et al. (2002) |
| *Gymnodinium sanguinem* | 82.6 % | Algae cells | Schlekat et al. (2002) |
| *Phaeodactylum tricornutum* | 80 % | Algae cells | Schlekat et al. (2002) |
| *Synechococcus* sp. | 78.3 % | Algae cells | Schlekat et al. (2002) |
| *Thalassiosira pseudonana* | 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, *P. tricornutum* | Lee et al. (2006) |

[a]This form of elemental selenium does not occur in nature and was synthesized in the laboratory



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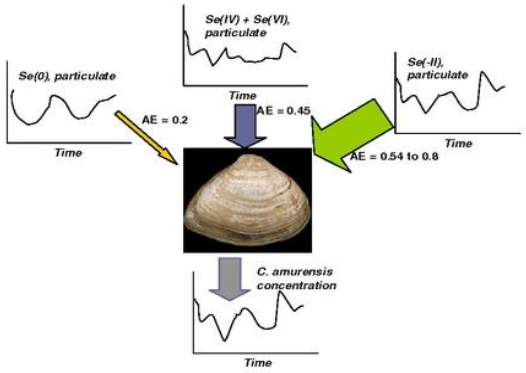


**Fig. 3** Bioaccumulation of particulate selenium in bivalves

Model Boundary Conditions and External Loads

*Riverine Inputs of TSM and Chlorophyll a*

Riverine inputs of flow from the Sacramento River at Rio Vista are daily records from the Interagency Ecological Program (IEP 2010) for the period of 1999–2008. The San Joaquin River is modeled as a tributary to the Sacramento River, with flow derived as the difference between Net Delta Outflow Index and flow from the Sacramento River at Rio Vista.

Riverine inputs (Sacramento and San Joaquin Rivers) of TSM and chlorophyll *a* were estimated as flow at the Sacramento River at Rio Vista and San Joaquin River multiplied by concentrations.

The riverine concentrations of TSM were modeled as a function of flow:

$$\mathrm{TSM}_{\mathrm{river}} = a + b * Q_{\mathrm{river}}{}^{c} \quad (2)$$

where $a$ is the minimum concentration in the river water, $b$ and $c$ are calibration coefficients, and $Q_{river}$ is the riverine flow rate.

Riverine chlorophyll *a* concentrations were observed data obtained from the USGS and Bay Delta and Tributary Project (BDAT) for the Sacramento River at Rio Vista for the period of 1999–2008. For the San Joaquin River, BDAT data for San Joaquin River at Twitchell Island were used.

*Selenium Loads from Refineries and Municipal and Industrial Wastewater*

Selenium loads to the NSFB include point sources from refineries, municipal and industrial dischargers and tributaries. Point and nonpoint sources of selenium were added to the model cells at their corresponding discharge locations (Table 1 in the ESM).

Daily refinery loads over 1999–2007 from five refineries in the NSFB estimated in Tetra Tech (2008) were used in the model calibration. For the refinery effluent data, only total selenium was reported, and for the purpose of the modeling, the speciation was held constant at values reported by Cutter and Cutter (2004): selenite (13 %), organic selenide (30 %), and selenate (57 %). The daily load varied from day to day depending on the effluent data reported and was 558.8 kg/year for 1999 for all five refineries combined.

Daily selenium loads from local tributaries estimated in a previous assessment (Tetra Tech 2008) 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 (USGS station 11458000). No selenium 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/year for 1999.

Selenium loads from other point sources including municipal and industrial wastewater discharges were also added to the model. Speciation for municipal wastewater discharges used is organic selenide (15 %), selenite (25 %), and selenate (60 %). For 1999, the total loads from these sources were 175.8 kg/year.

*Riverine Dissolved Selenium Loads*

Dissolved selenium loads for selenate, selenite, and organic selenide were specified from the rivers as a product of flow and selenium concentrations by species. Different species of selenium concentrations were derived using fitted functions



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based on observed data by Cutter and Cutter (2004) at the Sacramento and San Joaquin River stations, similar to the approach used in Meseck and Cutter (2006). A Delta removal constant was used in converting observed selenium concentrations in the San Joaquin River at Vernalis to concentrations at the confluence with Sacramento River. This constant represents exports of San Joaquin River through the aqueducts in the Delta and also the biogeochemical processes of selenium removal within the Delta.

*Particulate Selenium Loads*

Riverine particulates are assumed to exist in two forms: PSP and BEPS, the latter representing sediment bed-load transport. Riverine particulate selenium inputs are estimated as selenium concentrations associated with PSP and BEPS (both in micrograms per gram), multiplied by riverine inputs of PSP and BEPS (in milligrams per liter). Also added to the particulate loads are the riverine phytoplankton Se loads using a Se/C ratio and chlorophyll *a* concentrations.

Particulate selenium concentrations associated with PSP were measured by Doblin et al. (2006) and showed a range of values. Particulate elemental selenium ranged from 0.08 to 0.40 μg/g (mean, 0.149±0.108 μg/g), particulate selenite and selenate range from nondetectable to 0.25 μg/g (mean, 0.270±0.137 μg/g), and organic selenide concentrations ranged from 0.015 to 0.74 μg/g (mean, 0.134±0.238 μg/g) at Sacramento River at Rio Vista (Doblin et al. 2006). Particulate selenium concentrations associated with BEPS are data from Meseck and Cutter (2012). The total particulate selenium at Rio Vista is 0.46 μg/g (the sum of particulate organic, inorganic, and elemental selenium). Higher selenium content on particulates may be expected during low flows (e.g., 0.75 μg/g in November 1999). Therefore, the model was also run using a higher riverine particulate selenium concentration of 0.75 μg/g for a low flow period (river flow, $<1.5\times10^{10}$ l/day) (Table 3). Particulate selenium concentrations at the seawater end of the model domain observed by Doblin et al. (2006) ranged between 0.84 and 1.18 μg/g at Golden Gate Bridge. A seawater end member concentration for each species of particulate selenium was specified corresponding to measured values at Golden Gate.

Model Calibration and Evaluation

*Model Calibration*

Before the model is used to predict selenium concentrations on particulates and bivalves, it was calibrated for physical parameters (salinity and TSM), phytoplankton, and dissolved and particulate selenium species, using observed general water quality data (from cruises conducted by the USGS, http://sfbay.wr.usgs.gov/access/wqdata/) and selenium speciation data sampled by Cutter and Cutter (2004) for 1999. Calibration for the general water quality parameters was conducted based on data from 19 USGS monitoring stations located in the NSFB and was roughly on monthly intervals from January 1999 to December 1999. The use of the USGS dataset supplements data used in the previous study by Meseck and Cutter (2006), which was mainly based on Cutter and Cutter (2004) data. Selenium speciation data collected during two time periods in 1999 (April and November) by Cutter and Cutter (2004) were used in model calibration for selenium. Water year 1999 was selected for calibration because detailed refinery discharge data and selenium speciation data are available for this year, and selenium loads from refineries decreased by about two thirds in mid-1998 and have stayed at approximately those levels since that time. The 1999 estuary data thus represent conditions following refinery load reductions. Key model calibration parameters are those that affect advection and dispersion of PSP and BEPS, phytoplankton growth rate and grazing rate, selenium transformation rates, and Delta removal constants for selenium inputs from the San Joaquin River.

*Model Evaluation Criteria (Goodness of Fit)*

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).

$$\mathrm{GOF}(\%) = 100^{*}\left(1 - \left|\sqrt{\frac{\sum X_{\mathrm{cal}}}{\sum X_{\mathrm{obs}}}} - \sqrt{\frac{\sum X_{\mathrm{obs}}}{\sum X_{\mathrm{cal}}}}\right|\right) \qquad (4)$$

where $X_{\mathrm{cal}}$ is the model simulated concentration and $X_{\mathrm{obs}}$ is the

**Table 3** Lower and higher boundary of riverine and seawater endmember concentrations (Doblin et al. 2006; Meseck 2002; Baines et al. 2004)

| | Riverine boundary | | | | Seawater boundary |
|---|---|---|---|---|---|
| | PSP PSe (μg/g) | BEPS PSe (μg/g) | Se/C in phytoplankton (μg/g) | PSP PSe (μg/g) | Se/C in phytoplankton (μg/g) |
| Lower boundary | 0.46 | 0.25 | 15.9 | 0.84 | 21.0 |
| Higher boundary (applied when Net Delta Outflow Index, $<1.5\times10^{10}$ l/day) | 0.75 | 0.50 | 15.9 | 1.18 | 21.0 |



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observed concentration. A 100 % goodness of fit indicates a perfect fit between simulated and observed values.

*Model Evaluation*

The model evaluation was conducted using long-term data available for years after 1999, which include several low and high flow years, for the period of 1999–2008. The calibrated model was evaluated against estuarine profile data collected by USGS for salinity, TSM, and phytoplankton for two specific water years 2001 and 2005, and long-term total selenium data collected by the San Francisco Bay Regional Monitoring Program (RMP) for water year 2001 through water year 2007 (RMP 2010). The RMP dataset reports dissolved and total selenium and does not include characterization of selenium speciation and the separation of dissolved and particulate selenium. The difference between total and dissolved selenium, although in principle an approximation of particulate selenium, is not an accurate representation of particulate selenium, and sometimes negative values may result. 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 commonly used classification by the California Department of Water Resources (DWR 2010). The evaluation was for both simulations along the length of the estuary and at fixed locations over long-term time periods, for both physical and biological parameters and selenium species concentrations.

Model Hindcast

Model hindcasting 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 load reductions in 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 2010). Selenium loads of different species from the refineries for 1986 and 1998 were based on data from Meseck (2002).

## Results

Model Evaluation for the Post-1999 Period

The calibrated model was evaluated against estuarine profile data on salinity, TSM, and phytoplankton for water years 2001 and 2005 collected by USGS, and long-term total selenium data collected by RMP for water year 2001 through water year 2005 (RMP 2010). The water year 2001 represents a dry year, with flows much lower than 1999 and water year 2005 represents a relatively wet year, as noted above.

Evaluation of salinity, TSM, and chlorophyll *a* for the low flow year 2001 suggested good agreement of simulated salinity versus observed values for different months across the year (Figs. 1, 2, and 3 in the ESM). Overall values for goodness of fit for these months are between 71.5 and 97.9 % for salinity, 36.4 and 99.4 % for TSM, and 53.7 and 95.7 % for chlorophyll *a*. The location of the estuarine turbidity maximum (ETM) was simulated well for most months in 2001, particularly for June and July 2001. For about 2 months, chlorophyll *a* concentrations were under-predicted near the Central Bay, similar to the pattern in the calibration. For the evaluation period, the 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.

A similar evaluation of salinity, TSM, and chlorophyll *a* was performed for an above-normal flow year (2005) (Figs. 4, 5, and 6 in the ESM). Salinity predictions showed very good agreement with the observed data (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. For April and May 2005, the ETM was under-predicted (GOF=48.2–97.7 %). This is similar to the results in the calibration phase where the ETM was under-predicted on some occasions. Chlorophyll *a* predictions were able to represent the average values through the estuary but did not capture the peaks (GOF=25.2–98.5 %).

Simulated TSM and chlorophyll *a* concentrations were also evaluated for longer time periods at fixed locations, using data from the USGS long-term monitoring stations (Figs. 7 and 8 in the ESM). The model-simulated chlorophyll *a* and TSM concentrations were compared with long-term data at four stations, stations 3 (Suisun Bay), 6 (Suisun Bay), 14 (San Pablo Bay), and 18 (Central Bay), respectively. The results suggest that the model is able to capture the seasonal variations in chlorophyll *a* and TSM relatively well.

Although the calibration process for the general water quality parameters 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 1-D model in capturing the complexities of processes in the NSFB, and also to seasonal changes that were not fully parameterized during calibration.

Comparison of simulated selenium concentrations against the RMP transect sampling data for the period of 2000–2005 suggested that the model simulates profiles of



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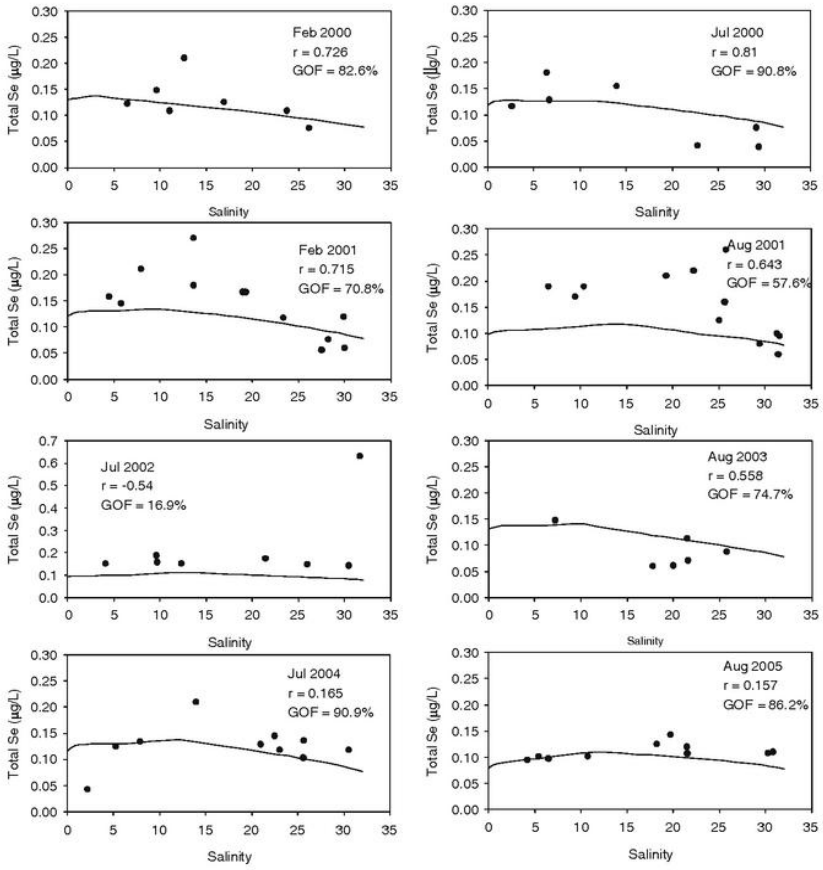


**Fig. 4** Model simulated total selenium concentrations (dissolved+particulate) compared with selenium data collected by the San Francisco Bay RMP. Note that the RMP dataset does not report selenium species information, and no selenium speciation data are available for this period in NSFB. RMP data on the Internet at: http://www.sfei.org/rmp/data

selenium concentrations along the estuarine longitude well for a range of hydrological and load input conditions during 2000–2005, including both dry and wet years, and dry and wet season conditions (Fig. 4), and the long-term variations in selenium concentrations at fixed locations (Fig. 5).

## Model Hindcast

The model hindcast (prior to refinery selenium load reductions) suggests that the model-simulated salinity, TSM and chlorophyll *a* compared well with the observed values for both high and low



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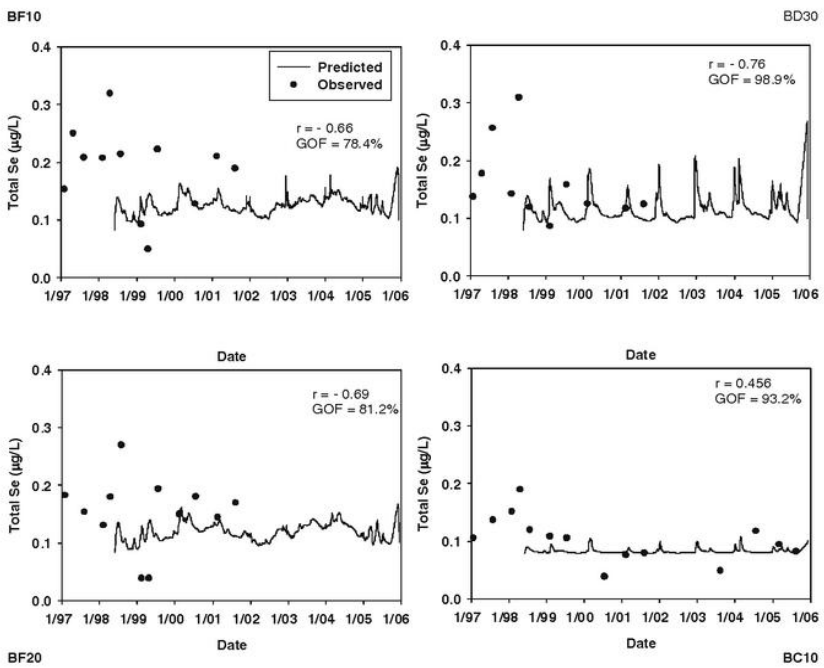


**Fig. 5** Model simulated total selenium concentrations at BF10 (Suisun Bay), BF20 (Suisun Bay), BD30 (San Pablo Bay), and at BC10 (Central Bay) compared with observed total selenium by RMP. RMP data on the Internet at: http://www.sfei.org/rmp/data

flow. The model is able to simulate the ETM that occurred during October 1998. The hindcast of dissolved selenium suggests that the model is able to simulate the relatively conservative mixing behavior of selenium during high flow periods and the mid-estuarine peaks during low flow, a result similar to that previously reported in Meseck and Cutter (2006). Simulated selenium concentrations on particulates for the hindcast period compared well with the observed particulate selenium values, and suggested that the model can represent the behavior of selenium on particulates in different periods (Fig. 6).

Simulated Selenium Concentrations on Particulates and Biota

Simulated selenium concentrations on particulate matter (in micrograms per gram) for 11 November 1999 were compared with the observed data from Doblin et al. (2006; Fig. 7). The predicted mean particulate selenium concentrations for NSFB for 11 November 1999 is 0.77±0.35 µg/g, compared with the observed value of 0.735±0.25 µg/g ($r$=0.45).

Predicted selenium concentrations in *C. amurensis* near Carquinez Strait as a function of time were compared with data from Stewart et al. (2004) and are shown in Fig. 8 for a range of ingestion rates and different assimilation efficiencies of organic selenium used.

Clam selenium concentrations are also available for a longer time period of 1995–2010 from USGS (Kleckner et al. 2010). Simulated clam selenium concentrations at Carquinez Strait for the time period prior to refinery load reductions (1995–1998) and following refinery load reductions (1999–2010) using an ingestion rate of 0.65 $gg^{-1}$ $day^{-1}$ and a seawater particulate selenium boundary of 1.05 µg/g were compared with these data (Fig. 9). The model is generally able to capture the seasonal and long-term patterns in clam selenium concentrations over a period with variability in hydrology and loading. Lower



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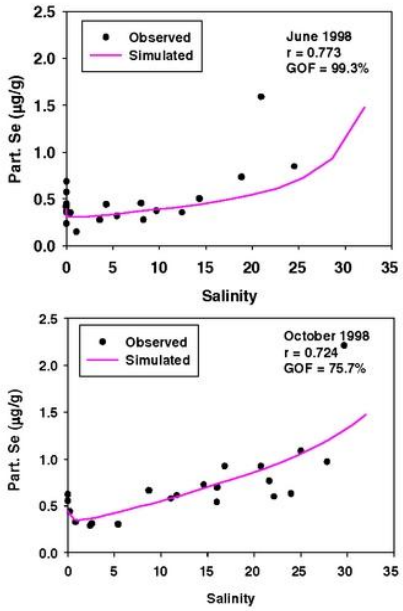


**Fig. 6** Model simulated hindcast values of particulate selenium for June and October 1998

selenium concentrations in bivalves are coincident with high flow periods (e.g., April) and wet years (e.g., 2005 and 2006).

Simulated selenium concentrations in muscle and liver tissues of white sturgeon and greater scaup using TTF and regression equations from Presser and Luoma (2006) were compared with observed values in the NSFB (Figs. 10 and 11). White sturgeon sampled from San Francisco Bay-Delta between 1986 and 1990 contained selenium at concentrations ranging from 9 to 30 µg/g dw (mean, 26.55 µg/g) in liver and 7 to 15 µg/g in muscle tissue (mean, 12.57 µg/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 µg/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 µg/g using a TTF of 1.3.

### Evaluation of Future Management Scenarios

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 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, it was assumed that the residence time of San Joaquin River water in the Delta significantly decreases, and, as a worst-case from the standpoint of selenium loading to NSFB, the Delta removal effect of selenium on San Joaquin River water was considered to be zero. Therefore, the scenario assumes higher inputs of selenium as a result of both increase in flow from the San Joaquin River and the loss of the Delta removal effects on selenium.

Model simulations using San Joaquin River flow at Vernalis were compared with 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- and low-flow periods (Fig. 12).

Predicted model-simulated selenium concentrations on particulates (in micrograms per gram) 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 µg/g predicted in the upper estuary (Fig. 12). These increases may lead to corresponding increases in clam concentrations. The application of this modeling framework to a wider range of loading and flow scenarios is presented in a technical memorandum developed as part of the selenium TMDL process (Tetra Tech 2010).

## Discussion

### Model Uncertainties

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 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 capture key aspects of physical and biological constituents that affect selenium concentrations. The model simulates salinity



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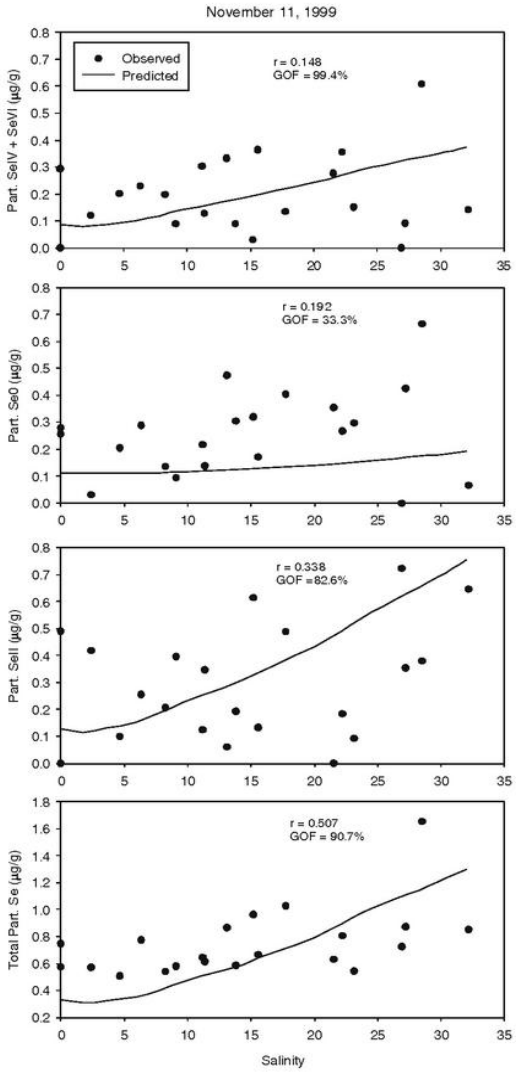


**Fig. 7** Simulated particulate selenium compared with the observed data from Doblin et al. (2006) for November 1999



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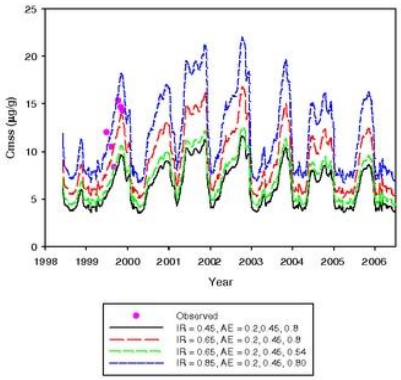


**Fig. 8** Simulated selenium concentrations in bivalve *C. amurensis* near the Carquinez Strait compared with observed values from Stewart et al. (2004; station 8.1)

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 1-D 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. This may be due to the method used for determining dissolved organic selenide (estimated as the difference of total dissolved selenium minus the dissolved selenite+selenate). Therefore the errors and uncertainty in the dissolved organic selenide may be larger. This also may be due to local variations in phytoplankton abundance and species, which may affect uptake of selenium and releases of dissolved organic selenium.

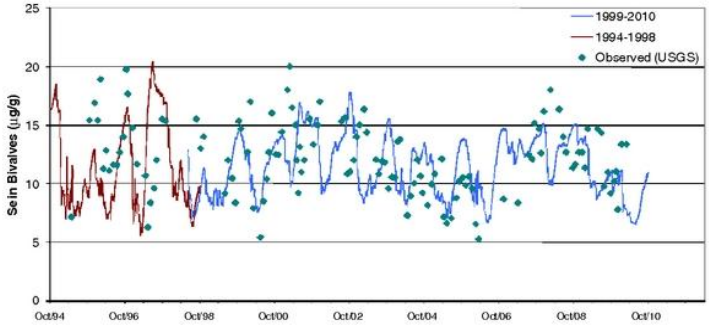


**Fig. 9** Simulated selenium concentrations in bivalve *C. amurensis* compared with long-term data from USGS at the Carquinez Strait for the period of 1995–2010 (Kleckner et al. 2010). Flow data used—DAYFLOW records from the California Department of Water Resources; refinery data used—daily data for 1999–2007, constant loads after 2007; San Joaquin River Selenium—observed data at Vernalis, multiplied by Delta removal constants with fixed speciation—selenite (SeIV), 0.028; Se(VI), 0.658; and OrgSe, 0.314



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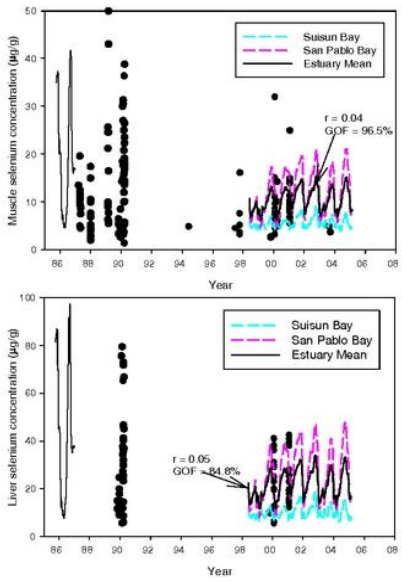


**Fig. 10** Simulated selenium concentrations in muscle tissue and liver of white sturgeon at Suisun Bay and San Pablo Bay compared with observed values (White et al. 1988, 1989; Urquhart et al. 1991, USGS and SFEI), using TTF = 1.3 for muscle tissue(Presser and Luoma 2010) and regression equation from Presser and Luoma (2006; for liver concentrations)

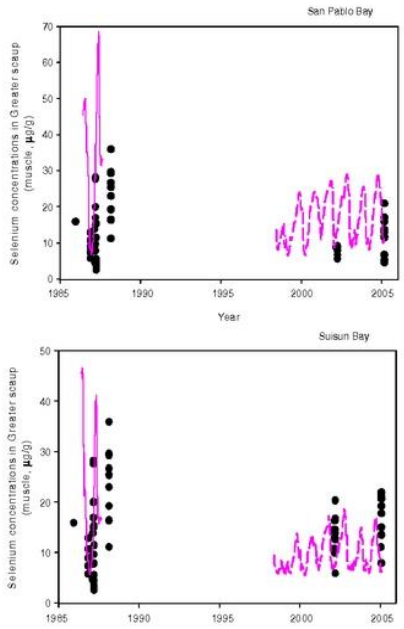


**Fig. 11** Simulated selenium concentrations muscle tissue of diving ducks (dry weight; Greater Scaup) compared with observed data in San Pablo Bay and Suisun Bay, respectively (White et al. 1988, 1989; Urquhart et al. 1991; SFEI), using TTF = 1.8

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 broad 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 with 33 cells representing a 100-km long modeling domain.

Future model development may seek to address some of the shortcomings of the modeling presented here, such as the occasional inability to represent the estuarine turbidity maximum and the chlorophyll *a* peaks, the uncertainties in riverine and ocean boundary conditions and their effect on the conclusions, and the difficulty in capturing large local-scale variability in organic selenium concentrations, which may be partly due to the complexity and limited understanding of phytoplankton growth dynamics and species distribution.

A sensitivity analysis of the various model parameters was performed. The analysis indicated that the model is relatively sensitive to parameters that affect the location and magnitude of the TSM. Dissolved and particulate selenium concentrations are most sensitive to the riverine input parameters (Table 3 in the ESM). Particulate selenium concentrations are sensitive to selenium content on particulates at the riverine boundary. Dissolved and particulate selenium are less sensitive to selenium transformation coefficients such as phytoplankton uptake and selenite adsorption rates. Particulate organic selenide and particulate selenium are also sensitive to increases in phytoplankton growth rates. The relatively high sensitivity of particulate organic selenium, particulate selenium, and dissolved selenite to increases in phytoplankton growth rate (also as an indicator of phytoplankton concentrations) underscores how certain species of selenium are closely tied to phytoplankton concentrations. In addition, particulate organic selenide is also sensitive



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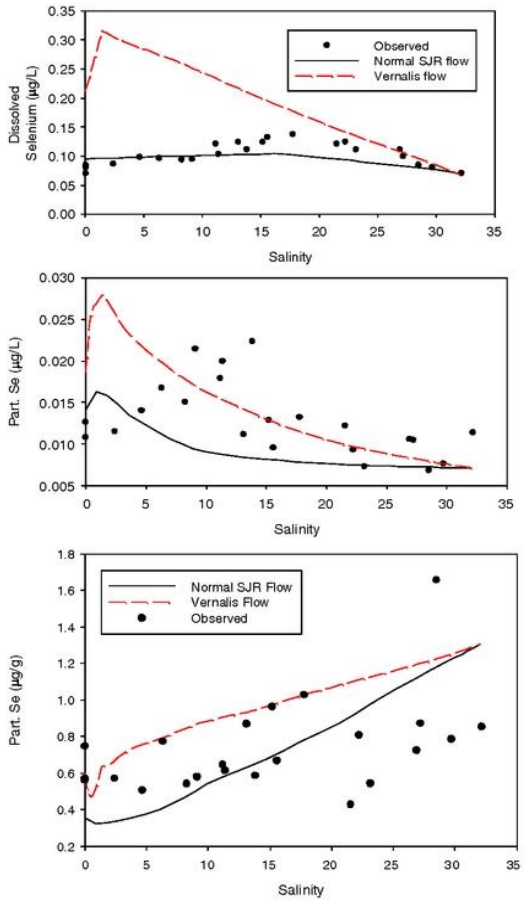


**Fig. 12** Predicted dissolved and particulate selenium for different San Joaquin River discharge rates during a low flow period (11 November 1999)

to its mineralization rate. Through adjustment of several of these parameters, the ECoS framework was able to capture the essential behavior of selenium and ancillary parameters in NSFB. Future work in the bay focusing on these components of selenium behavior, including characterization of the riverine boundary and phytoplankton growth and uptake, may enhance the robustness of the modeling.

Temporal Variations in Selenium Concentrations in Clams

The recently reported *C. amurensis* concentration data from San Francisco Bay (Kleckner et al. 2010) illustrate internannual and inter-seasonal patterns in clam concentrations from 1995 to 2010, a period over which there have been variations in freshwater inflows as well as changes in the



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selenium loading, particularly changes in refinery wastewater loading 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 observed 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 and inter-annual 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 is a feature of the clam data and cannot be explained by the dissolved selenium concentration data alone, as the dissolved data do not show a similar seasonal pattern. However, the modeling framework presented in this study does provide a plausible hypothesis, as outlined below. Particulates in the bay, especially phytoplankton, can have higher selenium concentrations (on a microgram-per-gram basis), than particulates originating in the riverine source in Rio Vista (with a greater mineral fraction). High flow periods are associated with high particulate loads from Rio Vista, largely made up of Sacramento River flows, resulting in lower average selenium concentrations in the bay than during low-flow periods. Thus, changes in selenium concentrations in clams from one year to the next appear to be influenced significantly by hydrology, with wet years (such as 2005 and 2006) resulting in lower clam concentrations. This hypothesis does not consider changes in the rate of selenium uptake as a function of the clam's life cycle, although such a process may also be a factor in the overall variation. There are, however, insufficient data to independently evaluate the significance of the growth effect at this time. An evaluation of the Kleckner et al. (2010) data showed no consistent relationships between clam size (as represented by mean shell length) and selenium concentrations. The hypothesis developed here through the integration of best-available data and modeling provides insight into the future management of selenium concerns in NSFB, although it must be re-evaluated as new data and process-level information become available.

The long-term trends in selenium concentrations in clams (1995–2010) suggest the importance of in-estuary transformations in affecting particulate and biota selenium concentrations in addition to the external loads. Given the decreases in external loads over the study period (both from the refineries and the San Joaquin River), dissolved selenium concentrations in the bay have shown a more direct response to these changes. However, the corresponding changes in particulate selenium are generally minimal, as reported previously in Doblin et al. (2006). As shown through the modeling framework presented here, this could be due to the fact that phytoplankton in the estuary are still able to concentrate relatively high selenium concentrations, which contribute to relatively high particulate selenium concentrations that enter the food web, and result in continued high concentrations in the clams. In effect, this framework indicates that particulate selenium concentrations, and therefore the concentrations in filter feeders, such as clams, are not a simple linear function of dissolved concentrations. Accurate predictions of concentrations in the food web require accurate characterization of particulate concentrations, through observations where possible, or through adequate characterization of uptake by the particulate phases. The model developed here is a tool for supporting such predictions.

## Summary and Conclusions

The ECoS model framework was applied to the NSFB for computing salinity, TSM, and chlorophyll *a*, and for selenium concentrations. The model was calibrated to data from 1999, because this is the most recent year for which speciated selenium data in the water column of the NSFB are available. The three ancillary constituents, salinity, TSM, and chlorophyll *a*, were calibrated using monthly water quality cruise data reported by the USGS. Although the ancillary water quality data in the bay are relatively abundant for the calibration of a 1-D model, the calibration period was limited by the availability of selenium data. Following calibration, where model parameters, especially the first-order rate constants that represent selenium transformation and uptake were estimated, the model was applied to different years for evaluating its performance. The calibrated model performed well under different hydrological and load conditions, and was able to simulate salinity, TSM, and chlorophyll *a* profiles for both dry years (e.g., 2001) and wet years (2005), and long-term TSM and chlorophyll *a* concentrations variations. The calibrated model was also run in a hindcast mode using hydrological and refinery loads for 1998. Selenium species and loads in this period were different from current loads, and the hindcast was another test of the credibility of the model. The simulated dissolved selenium concentrations compared well with the observed data. The model was able to simulate the mid-estuarine peaks in selenite for low flow of 1998. This indicates 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.

The model was able to simulate different selenium speciation and the bioavailability of each species, therefore is able to simulate selenium concentrations on particulates relatively well for different time periods (e.g., 1999 and 1998). The model could also represent the long-term variations (inter-annual and seasonal) in clam selenium concentrations for both prior-to refinery clean up (1994–1998) and post-refinery clean



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up time periods (1998–2010), including years with high and low clam selenium concentrations. The accumulation of selenium to higher trophic organisms is simulated using a TTF approach, which is able to represent selenium concentrations in white sturgeon and greater scaup in the bay.

A scenario of increasing flow and selenium loads from the San Joaquin River was also examined using the calibrated model. The results suggest that when flow from the San Joaquin River is a greater contributor to outflow from the Delta, significant increases in dissolved and particulate selenium, and selenium on particulates, are predicted in the bay. This would be expected to increase clam concentrations. This is of interest for long term planning for selenium management in NSFB, because there are plans being evaluated by the state of California to make changes in the way water is exported from the Delta through intakes further upstream in the Sacramento River, and by use of an isolated conveyance facility (CALFED 2008). Manipulations to the Delta system, especially those that increase San Joaquin flow into the bay, will also have selenium impacts to the bay that must be evaluated.

Although simplified through a 1-D representation, the modeling approach presented here is able to capture key features of selenium behavior at a level of complexity that is consistent with data that can be measured in the bay in future years. A benefit of the model is its ability to link sources to biota concentrations under a range of hydrologic conditions, and with mechanistic representations of transport, transformation and uptake processes. The mechanistic representation allows consideration of selenium uptake under future conditions, with changes in background water quality, hydrology, and the food web structure, which may be related to human interventions or natural causes. The modeling framework as developed, or with changes to reflect underlying processes and Delta modifications, can be used to explore selenium management options in San Francisco Bay in the context of the TMDL.

**Acknowledgments** We thank J.R.W. Harris for providing a copy of the ECoS modeling framework for this application. We thank Nicholas Fisher, Samuel Luoma, Regina Linville, and John Oram for serving as reviewers during the model development process and appreciate the comments of two anonymous reviewers of the manuscript. These inputs have strengthened the analysis and presentation of this work. Financial support for LC, SBR, and TMG was provided by the Western States Petroleum Association. Opinions expressed in the paper are those of the authors and not of the agencies they are employed by or of the funding entity.

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## No comments

- n/a -

***No comments***

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# APPENDIX D
# TOXINS

## WORKING DRAFT
## BAY DELTA CONSERVATION PLAN

**January 2012**

ICF INTERNATIONAL

## *No comments*

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Appendix D
# Toxins

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***No comments***

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***No comments***

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# Figures

**Appear at the end of the appendix.**

Figure D-1 Generic Conceptual Model to Evaluate Preliminary Proposal Toxins Effects
Figure D-2 Methylmercury Cycling in Aqueous System

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## *No comments*

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# Acronyms and Abbreviations

| | |
|---|---|
| µg/g | micrograms per gram |
| µg/L | micrograms per liter |
| AWQC | ambient water quality criteria |
| Bay-Delta | San Francisco Bay–Sacramento–San Joaquin River Delta |
| BDCP | Bay-Delta Conservation Plan |
| cfs | cubic feet per second |
| CM | Conservation Measure |
| CRT | Criterion Total Recoverable |
| Cu | copper |
| $Cu^{2+}$ | cupric ion |
| DBW | California Department of Boating and Waterways |
| DDD | Dichlorodiphenyldichloroethane |
| DDE | Dichlorodiphenyldichloroethene |
| DDT | Dichlorodiphenyltrichloroethane |
| Delta | Sacramento–San Joaquin River Delta |
| DOC | dissolved organic carbon |
| DRERIP | Delta Regional Ecosystem Restoration Implementation Plan |
| EDC | Endocrine-disrupting compounds |
| EEQ | estradiol equivalent |
| EIS/EIR | environmental impact statement/environmental impact report |
| EPA | U.S. Environmental Protection Agency |
| FRV | Final Residual Value |
| kg/yr | kilograms per year |
| LLT | late-long-term |
| ng/L | nanograms per liter (equivalent to1 part per trillion, or ppt) |
| NH3+ | ammonia (also referred to as un-ionized ammonia) |
| NH4+ | ammonium ion |
| NMFS | National Marine Fisheries Service |
| NPDES | National Pollutant Discharge Elimination System |
| NTR | National Toxics Rule |
| OEHHA | Office of Environmental Health Hazard Assessment |
| PCBs | Polychlorinated biphenyls |
| POD | pelagic organism decline |
| ROAs | restoration opportunity areas |
| Se | selenium |
| $Se^{2-}$ | selenides |
| $Se^{4+}$ | selenites |
| $Se^{6+}$ | selenates |
| TMDL | total maximum daily load |
| USFWS | U.S. Fish and Wildlife Service |
| USGS | U.S. Geological Survey |
| WWTP | wastewater treatment plant |

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## *No comments*

- n/a -

# Appendix D
# Toxins

## D.1 Executive Summary

Toxins have been identified as adverse stressors in the Delta ecosystem and have been associated with pelagic organism decline (POD) (Baxter et al. 2010; Glibert 2010; Glibert et al. 2011). Some of these toxins are contaminants that have been introduced to the ecosystem, and others are naturally occurring constituents in the Delta that have been mobilized and/or concentrated by anthropogenic activities. Although contaminants in water can be directly lethal to biota at very high concentrations, toxins usually occur at concentrations much below lethal levels, enter the food chain at lower trophic levels, and can become more concentrated higher up in the food chain. Sublethal levels in fish result in various effects, including impaired growth and reproduction, and increase in the organism's susceptibility to disease (Werner et al. 2008).

The preliminary proposal (PP) will not introduce new toxins or increase the concentrations of toxins in the Plan Area directly. , with the exception of herbicides, which would be applied in limited and safe concentrations to control invasive aquatics weeds. However, the PP includes restoration and changes in water operations that have the potential to change how toxins already present in the Plan Area are mobilized and transported in the Plan Area . To determine whether PP actions would influence the exposure to and effects of toxins on covered fish species, potential mechanisms for PP actions to result in increased concentrations and bioavailability of toxins first were identified and evaluated. This was achieved by developing conceptual models that included all factors that influence the environmental fate and transport, mobility in an aquatic system, and bioavailability to covered fish species for each toxin. Quantitative analyses are applied where they were useful in describing factors within the conceptual models, and if data inputs and available analytical and modeling tools were deemed sufficient to provide reliable results. As discussed in this appendix, given the complex nature of toxin biogeochemistry, area hydrology, and behavior and physiology of covered fish species that together determine the effects of toxins, quantitative analyses alone were not sufficient to fully examine potential effects. The environmental toxins evaluated in this appendix were selected based on historical and current land use along with published literature regarding water quality in the Delta and the types of toxins that have effects on fish.

- Mercury and methylmercury
- Selenium
- Copper
- Ammonia/um
- Pesticides
  - Pyrethroids
  - Organochlorines
  - Organophosphates

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***No comments***

- n/a -

Based on results of the evaluation presented in this appendix, PP water operations are not expected to affect toxins significantly in the Sacramento–San Joaquin River Delta (Delta) through either increased mobilization or transport. Two primary pathways of effects on toxins were examined in connection with water operations, an increase in the proportional amount of flow from the San Joaquin River and a reduction in flow in the Sacramento River.

The first pathway is the potential for increased loading of selenium from increased contributions of water from the San Joaquin watershed as Sacramento River inputs were diverted by north Delta intakes. Based on the evaluation of current and expected future reductions in selenium from the San Joaquin watershed, and source-water fingerprinting that indicates no increase of San Joaquin water contribution at Suisun Marsh and a only a slight increase in the south Delta, minimal effects on selenium or associated effects on covered fish species are expected.

The second issue connected to PP water operations is the potential for decreased dilution capacity of the Sacramento River, especially for Sacramento Regional Wastewater Treatment Plant (WWTP) effluent, and more specifically for ammonia and pyrethroids. Modeling results presented in Appendix C indicate that reduced dilution capacity in the Sacramento River at the Sacramento WWTP will result from changes in upstream reservoir operations associated with the PP, not from diversion of water to the Yolo Bypass or from north Delta intakes located downstream of the WWTP. Quantitative analysis presented in this appendix indicates that the Sacramento River will have sufficient dilution capacity under the PP for both ammonia and pyrethroids to avoid adverse effects from these toxins on the covered fish.

Restoration actions will result in some level of mobilization and increased bioavailability of methylmercury, copper, and pesticides (including organophosphate, organochlorine and pyrethroid pesticides). Given current information, it is not possible to estimate the concentrations of these constituents that will become available to covered fish species, but review of the conceptual models for each of these toxins indicates that the effects should be limited both temporally and spatially. The most problematic of these potential effects is methylmercury. To address this issue, the Plan includes Conservation Measure (CM) 12 Methylmercury Management, which provides for site-specific assessment of restoration areas, integration of design measures to minimize methylmercury production, and site monitoring and reporting. The areas with the highest potential for methylmercury generation are the Yolo Bypass, and to a lesser extent, the Mokelumne-Cosumnes River. With the implementation of CM12, effects of methylmercury mobilization on covered fish at the tidal wetland restoration sites are expected to be minimized.

In general, the following conclusions can be drawn.

- Preliminary proposal water operations will have few to no effects on toxins in the Delta.
- Preliminary proposal restoration will increase bioavailability of certain toxins, especially methylmercury, but the overall effects on covered fish species are expected to be localized and of low magnitude.
- Available data suggest that species exposure to toxins would be below sublethal and lethal levels.
- The long-term benefits of restoration will reduce exposure to existing toxins in the environment and eliminate sources.

A summary of conclusions from the toxins analysis is presented in Table D-1. The color coding in the table is based on consideration of the potential for an increase in the bioavailability of toxins due to



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## *No comments*

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preliminary proposal actions, presence of covered fish species/life stages, and expected potential for effects on covered species/life stage. Based on this analysis, none of the scenarios was rated as *High* potential for effects.

- **None—**Areas with potential for increase in toxins due to the PP, but susceptible life stage of covered species is absent (also applies if there is fish occurrence, but no toxins).
- **Low—**Areas with potential for increase in toxins due to PP and susceptible life stage of covered species present, but evaluation shows little potential for effects.
- **Moderate—**Same as *Low*, but evaluation shows moderate potential for effects.
- **High—**Same as *Moderate*, but evaluation shows high potential for effects based on mobilization of toxins into the foodweb and effects on covered fish species.

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## *No comments*

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Table D-1. Potential for Effects of Toxins on Covered Fish Species from the Preliminary Proposal

| Species | Life Stage | BDCP Regions | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | Yolo Bypass | Cache Slough | North Delta | West Delta | Suisun Bay | Suisun Marsh | East Delta | South Delta |
| Delta smelt | Eggs | M, C | M, C | C, S, P* | C, S, P | | M, S* | M* | S, P* |
| | Larva | M, C | M, C | C, S, P* | C, S, P | S | M, S* | M* | S, P* |
| | Juvenile | M, C | M, C | C, S, P* | C, S, P | S | M, S* | M* | S, P* |
| | Adult | M, C | M, C | C, S, P* | C, S, P | S | M, S* | M* | S, P* |
| Longfin smelt | Eggs | M, C | M, C | C, S, P* | C, S, P | | M, S | | |
| | Larva | M, C | M, C | C, S, P* | C, S, P | S | M, S | M* | S, P |
| | Juvenile | M, C | M, C | C, S, P* | C, S, P | S | M, S | | S, P |
| | Adult | M, C | M, C | C, S, P* | C, S, P | S | M, S | | S, P |
| Steelhead | Egg/Embryo | | | | | | | | |
| | Fry | | | | | | | | |
| | Juvenile | M, C | M, C | C, S, P | C, S, P | S | M, S | M | S, P |
| | Adult | M, C | M, C | C, S, P | C, S, P | S | M, S | M | S, P |
| Winter-run Chinook salmon | Egg/Embryo | | | | | | | | |
| | Fry | M, C | M, C | C, S, P | C, S, P | | | | |
| | Juvenile | M, C | M, C | C, S, P | C, S, P | S | M, S | M | S, P |
| | Adult | M, C | M, C | C, S, P | C, S, P | S | M, S | M | |
| Spring-run Chinook salmon | Egg/Embryo | | | | | | | | |
| | Fry | M, C | M, C | C, S, P | C, S, P | | | | |
| | Juvenile | M, C | M, C | C, S, P | C, S, P | S | M, S | M | S, P |
| | Adult | M, C | M, C | C, S, P | C, S, P | S | M, S | M | |
| Fall-/late fall-run Chinook salmon | Egg/Embryo | | | | | | | | |
| | Fry | M, C | M, C | C, S, P | C, S, P | S | M, S | M | S, P |
| | Juvenile | M, C | M, C | C, S, P | C, S, P | S | M, S | M | S, P |
| | Adult | M, C | M, C | C, S, P | C, S, P | S | M, S | M | S, P |

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***No comments***

- n/a -

| Species | Life Stage | BDCP Regions | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | Yolo Bypass | Cache Slough | North Delta | West Delta | Suisun Bay | Suisun Marsh | East Delta | South Delta |
| Sacramento splittail | Egg/Embryo | M | | C, S, P* | | | M, S | M | S, P |
| | Larvae | M | | C, S, P* | | | M, S | M | S, P |
| | Juvenile | M | M | C, S, P* | C, S, P | S | M, S | M | S, P |
| | Adult | M | M | C, S, P* | C, S, P | S | M, S | M | S, P |
| White sturgeon | Egg/Embryo | | | | | | | | |
| | Larva | M | M | C, S, P* | C, S, P | | | M | S, P |
| | Juvenile | M | M | C, S, P* | C, S, P | S | M, S | M | S, P |
| | Adult | M | M | C, S, P* | C, S, P | S | M, S | M | S, P |
| Green sturgeon | Egg/Embryo | | | | | | | | |
| | Larva | | | | | | | | |
| | Juvenile | M, C | M, C | C, S, P* | C, S, P* | S* | M, S* | M* | S, P* |
| | Adult | M, C | M, C | C, S, P* | C, S, P* | S* | M, S* | M* | S, P* |
| Pacific lamprey | Egg/Embryo | | | | | | | | |
| | Ammocoete | M, C | M, C | C, S, P* | C, S, P* | | | M | S, P* |
| | Macropthalmia | M, C | M, C | C, S, P* | C, S, P* | S* | S* | M* | S, P* |
| | Adult | M, C | M, C | C, S, P* | C, S, P* | S* | M, S* | M* | S, P* |
| River lamprey | Egg/Embryo | | | | | | | | |
| | Ammocoete | M, C | M, C | | | | | M | |
| | Macropthalmia | M, C | M, C | C, S, P* | C, S, P* | S* | M, S* | M* | S, P* |
| | Adult | M, C | M, C | C, S, P* | C, S, P* | S* | M, S* | M* | S, P* |

* Scoring partially based on low abundance of species/life stage in the area.
M = mercury, P = pesticides, S = selenium, C = copper
Categories of effect of toxin as result of BDCP:

| | |
|---|---|
| | None |
| | Low |
| | Medium |
| | High |

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***No comments***

- n/a -

## D.2 Organization of Appendix

This appendix presents a discussion of the toxins that are widely recognized as significant to determining the potential of the Delta ecosystem to support covered fish species, and how potential changes to toxins caused by the preliminary proposal could affect covered fish species. To do this, the appendix provides a general overview of toxic constituents currently present in the Delta aquatic ecosystem, identifies and assesses changes in toxins that could result from implementation of the preliminary proposal, and describes how those changes could result in changes in exposure of covered fish species to toxins. The analysis focuses only on changes in toxins that are directly attributable to the preliminary proposal actions that could affect covered fish species.

Water quality parameters, including salinity, turbidity, and temperature, are integrated with the hydrologic flow analyses and are discussed in Appendix C. Results of the flow analysis are included in this appendix where they support analysis of toxins. This appendix discusses only covered fish species. Ecological effects, including food chain and organisms other than covered fish species, are evaluated in Appendix F, *Ecological Effects*.

The approach in this toxins analysis is to develop a complete picture of all factors that contribute to the bioavailability and effects of these toxins on covered fish species. Qualitative conceptual models are presented that capture and describe all determining factors. The conceptual models draw from those developed by the Delta Regional Ecosystem Restoration Implementation Plan (DRERIP), along with other relevant information sources. Quantitative analyses are used where they are useful in describing factors within the conceptual models, and if data inputs and available analytical and modeling tools are deemed sufficient to provide reliable results. As discussed in this appendix, given the complex nature of toxin biogeochemistry, area hydrology, and behavior and physiology of covered fish species that together determine the effects of toxins, quantitative analyses alone were not sufficient to fully examine potential effects.

The analyses in this appendix are presented in two steps. The first step identifies effects on toxins that are directly attributable to preliminary proposal actions. The second step evaluates the potential for these changes in toxins to affect covered fish species, at what life stages, and where in the preliminary proposal study area. The general approach to the analysis for each toxic constituent is outlined below.

1. Determine effects of preliminary proposal actions on potentially toxic constituents in the Delta ecosystem.
    a. Describe the environmental chemistry of each parameter, the source of the element, how it is transported in the environment, and where it tends to accumulate.
    b. Discuss preliminary proposal actions that could result in changes in toxic water constituents, at what locations and when (if there is a seasonal component).
2. Determine effects of changes in potentially toxic constituents on covered fish species.
    a. Compare the spatial/temporal occurrence of each covered fish species/life stage with changes in toxins, identifying where changes in toxins coincide temporally and spatially with the presence of covered fish species.
    b. Discuss how preliminary proposal–induced changes to toxins could affect covered fish species/life stages in the Delta.



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***No comments***

- n/a -

## D.3 Overview of Toxins as Stressors

Stressors act on the environment by changing flow, water quality, temperature, or other attributes that determine the suitability of habitat for a species. Toxins have been identified as adverse stressors in the Delta ecosystem and have been associated with POD (Baxter et al. 2010; Glibert 2010; Glibert et al. 2011). Some of these toxins are contaminants that have been introduced to the ecosystem, and others are naturally occurring constituents in the Delta that have been mobilized and/or concentrated by anthropogenic activities. Although contaminants in water can be directly lethal to biota at very high concentrations, contaminants usually occur at concentrations much below lethal levels, enter the food chain at lower trophic levels, and can become more concentrated higher up in the food chain. Sublethal levels in fish result in various effects, including impaired growth and reproduction, and increase in the organism's susceptibility to disease (Werner et al. 2008).

### D.3.1 Selection of Toxin Stressors for Analysis

Water quality characteristics and the presence of contaminants (toxins) in the environment are determined by both natural conditions and land use. The primary land uses affecting toxins in the Delta include historical mining operations in the mountains drained by Delta tributaries, agriculture in the Delta and tributaries, discharges related primarily to rural human habitation (wastewater), and discharges related to urban development (stormwater runoff, municipal wastewater, industrial wastewater). The types of contaminant issues typically associated with these land uses are presented in Table D-2 and discussed further in the following paragraphs.

**Table D-2. Land Use and Typically Associated Contaminant Issues**

| Land Use | Typical Discharges/Operations | Typical Contamination Issues |
|---|---|---|
| Mining (historical) | Concentrated mining waste | Mercury and copper (specific to mining operations local to Delta) |
| Agriculture | Fertilizers | Nutrients (ammonia) |
| | Pesticides | Copper |
| | Drainage | Pesticides |
| | | Selenium* |
| Rural human habitation | Wastewater discharge | Nutrients (ammonia) |
| Urban development | Municipal wastewater treatment plant discharge | Nutrients (ammonia), pesticides, endocrine disruptors |
| | Stormwater runoff | Metals, pesticides, petroleum residues (PAHs) |
| | Industrial waste discharges | Metals, PCBs (from historical discharges) |
| * Selenium from agricultural drainage is specific to locations like the Delta that have high levels of naturally occurring selenium in soils, which are concentrated in agricultural drainage. | | |

Historical mining of mercury and gold resulted in concentrating and mobilizing certain metals that occur naturally in the mountains of the upper tributaries. Metals are present in rocks, soils, and sediments to varying degrees, dependent on the source rocks. During the mining process, naturally occurring metals were mobilized, transported via streams, and deposited in sediments of the Delta marshes, wetlands, and streambeds.



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Agriculture has been the primary land use in the Delta for more than a century (Wood et al. 2010). In the Plan Area, 503,779 acres (59%) are used for agriculture (see Chapter 2, *Existing Conditions*). The pesticides, herbicides, and fertilizers applied to agricultural lands throughout the Delta are present in the soils where they were applied but also have migrated off the farmed properties via air, groundwater, runoff, and rivers and are dispersed throughout all environmental media in the Delta ecosystem. The majority of pesticides used in the Delta fall into three families of pesticides—organochlorides (including dichlorodiphenyltrichloroethane [DDT]) were used historically and now are banned, and pyrethroids and organophosphates are currently in use.

Rural developments associated with agricultural land use have minimal discharge of toxins. The main types of discharges are relatively small volumes of wastewater, typically through local septic systems.

Cities and towns account for only 8% of the Plan Area (70,174 acres). The main urban centers are the cities of Sacramento and West Sacramento located on the Sacramento River, and the city of Stockton located on the San Joaquin River (Wood et al. 2010). Although urban development accounts for a small percentage of land use in the Delta, urban discharges have affected the aqueous environment. Release of toxins to water typically associated with urban development is related to stormwater and WWTP discharges.

Stormwater typically is characterized by varying levels of metals, pesticides, and hydrocarbons that can accumulate in river sediments over time. Historically, polychlorinated biphenyls (PCBs) often were associated with urban discharge, and these contaminants have been detected in fish tissues in San Francisco Bay, although there is little research on PCB levels in the Delta.

Wastewater discharges from WWTPs also are associated with urban and suburban land use. Wastewater contains high levels of nutrients, and the concentrations in effluent are dependent on the level of the treatment system. In the Delta, ammonia historically has been problematic in both the Sacramento and San Joaquin Rivers; however, planned and functioning upgrades to WWTPs have resulted or will result in reductions in ammonia (discussed later in this appendix). Both stormwater runoff and effluent from the Sacramento WWTP have been shown to contain pesticides, including pyrethroids (Weston et al. 2010). Although this will be discussed further, it should be noted that the north Delta intakes are downstream of the Sacramento WWTP discharge and would not affect dilution of effluent.

Endocrine-disrupting compounds (EDCs), which include many of the pesticides, are also referred to as *emerging contaminants* and also are found in urban runoff and wastewater discharges. EDCs include many different types of chemicals from a wide range of sources with widely varying chemical attributes, and their distribution in the Delta is not yet fully understood.

The environmental toxins discussed in this appendix were selected based both on land use discussed above and on other literature that identifies primary constituents of concern to fish in the Delta. The U.S. Environmental Protection Agency (EPA) identified ammonia, selenium, pesticides, and contaminants of emerging concern (including endocrine disruptors) for more focused evaluation in *Water Quality Challenges in the San Francisco Bay/Sacramento–San Joaquin Delta Estuary* (U.S. Environmental Protection Agency 2011). Toxins of concern also are identified under the Clean Water Act Section 303(d) list provided in Table D-3. Those for which total maximum daily load (TMDL) studies have been completed are listed in Table D-4. These lists identify the same toxins listed above plus furans, dioxins, PCBs, mercury/methylmercury, and pathogens. Dioxin, furans, and pathogens are listed only for Stockton, and *E. coli* (a pathogen) is listed for the east Delta.



## *No comments*

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**Table D-3. Clean Water Act 2010 Section 303(d) Listed Pollutants and Sources in the Plan Area**

| Pollutant/Stressor | Listing Region | Listed Source | Delta Location of Listing |
|---|---|---|---|
| Chlordane | Central Valley | Agriculture, Nonpoint Source | N, W |
| Chlorpyrifos | Central Valley | Agriculture, Urban Runoff/Storm Sewers | N, S, E, W, NW, C, Exp, Stk |
| DDT | Central Valley | Agriculture, Nonpoint Source | N, S, E, W, NW, C, Exp, Stk |
| Diazinon | Central Valley | Agriculture, Urban Runoff/Storm Sewers | N, S, E, W, NW, C, Exp, Stk |
| Dioxin Compounds | Central Valley | Source Unknown, Atmospheric Deposition | Stk |
| E. Coli | Central Valley | Source Unknown | E |
| Invasive Species | Central Valley | Source Unknown, Ballast Water | N, S, E, W, NW, C, Exp, Stk |
| Furan Compounds | Central Valley | Contaminated Sediments, Atmospheric Deposition | Stk |
| Group A Pesticides[a] | Central Valley | Agriculture | N, S, E, W, NW, C, Exp, Stk |
| Mercury | Central Valley | Resource Extraction | N, S, E, W, NW, C, Exp, Stk |
| Pathogens | Central Valley | Recreational and Tourism Activities (non-boating), Urban Runoff/Storm Sewers | Stk |
| PCBs | Central Valley | Source Unknown | N, Stk |
| Unknown Toxicity[b] | Central Valley | Source Unknown | N, S, E, W, NW, C, Exp, Stk |
| Electrical Conductivity | Central Valley | Agriculture | S, W, NW, Stk |
| Organic Enrichment/ Low Dissolved Oxygen | Central Valley | Municipal Point Sources, Urban Runoff/Storm Sewers | Stk |
| Sediment Toxicity | Central Valley | Agriculture | E |
| Total Dissolved Solids | Central Valley | | S |

Source: <http://www.waterboards.ca.gov/water_issues/programs/tmdl/2010state_ir_reports/category5_report.shtml>. Accessed: November 16, 2011.

DDT = dichlorodiphenyltrichloroethane , PCB = polychlorinated biphenyls.

Delta Locations: C = central, E = east, Exp = export area, N = north, NW = northwest, S = south, STK = Stockton Deep Water Ship Channel, W = west.

[a] Group A pesticides include aldrin, dieldrin, chlordane, endrin, heptachlor, heptachlor epoxide, BHC (including lindane), endosulfan, and toxaphene.

[b] Toxicity is known to occur, but the constituent(s) causing toxicity is unknown.

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## *No comments*

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**Table D-4. Summary of Completed and Ongoing Total Maximum Daily Loads in the Delta**

| Pollutant/Stressor | Water Bodies Addressed | Total Maximum Daily Load Status |
|---|---|---|
| Chlorpyrifos and Diazinon | Sacramento County urban creeks | TMDL report completed—September 2004<br>State-federal approval—November 2004 |
| | Sacramento and San Joaquin Rivers and Delta | TMDL report completed—June 2006<br>State-federal approval—October 2007 |
| | Sacramento and Feather Rivers | TMDL report completed—May 2007<br>State-federal approval—August 2008 |
| | Lower San Joaquin River | TMDL report completed—October 2005<br>State-federal approval—December 2006 |
| Methylmercury | Delta | TMDL report completed—April 2010 |
| Pathogens | Five-Mile Slough, Lower Calaveras River, Mormon Slough, Mosher Slough, Smith Canal, and Walker Slough | TMDL report completed—March 2008<br>State-federal approval—May 2008 |
| Pesticides | Central Valley | Ongoing |
| Organochlorine Pesticides | Central Valley | Ongoing |
| Salt and Boron | Lower San Joaquin River | TMDL report completed—October 2005<br>State-federal approval—February 2007 |
| Selenium | San Joaquin River | TMDL report completed—August 2001<br>State-federal approval—March 2002 |
| Low Dissolved Oxygen | Stockton Deep Water Ship Channel | TMDL report completed—February 2005<br>State-federal approval—January 2007 |
| Source: <http://www.swrcb.ca.gov/water_issues/programs/tmdl/#rb5>. Accessed: November 17, 2011. | | |

The environmental toxins evaluated in this appendix were selected based on historical and current land use along with published literature regarding water quality in the Delta and the types of toxins that have effects on fish.

- Mercury and methylmercury
- Selenium
- Copper
- Ammonia/um
- Pesticides
  - Pyrethroids
  - Organochlorines
  - Organophosphates

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## *No comments*

- n/a -

## D.4 Methods

To evaluate effects on covered species, published data on occurrence, biogeochemical behavior, mass balances, quantitative modeling tools, and studies of impacts of specific toxic constituents on covered fish species were reviewed. There are a broad range of available studies specific to the Central Valley and Delta region, many of which are referenced in this appendix. The objective of the analysis in this appendix is to provide an overview of how these constituents could become more bioavailable to covered fish species in the Plan Area and whether there is potential for preliminary proposal actions to result in effects on covered species.

A qualitative framework or conceptual model is presented to evaluate the potential effects of BDCP conservation measures on toxins in the Delta environment, and the possible effects on covered fish species. The effects on covered fish species are dependent more on the increase in both bioavailability and concentration of a given toxin than on just the increase in concentration of the toxin in the water. Given the currently available analytical tools, available occurrence data, and the breadth of the Plan Area, a purely quantitative approach is unable to capture the environmental/ chemical factors that result in transformation of a chemical to a form that is more bioavailable and toxic in the ecosystem. Where available field data and quantitative modeling tools were deemed sufficient to capture the relevant aspects of the constituent in estimating impacts, quantitative model results are presented along with a full discussion of the conceptual model for each constituent. Where quantification would lead to results with very high margins of error and uncertainty and would not appropriately inform or define the effects on covered species, effects were discussed only qualitatively with the objective of determining the probability of effects on covered species.

For reference, the EPA Ambient Water Quality Criteria (AWQC) for chronic exposures (AWQC-Fresh Water-Chronic) are included in the discussions of each toxin for context. The AWQC-Fresh Water-Chronic is expressed as the highest concentration of a substance in surface water to which an aquatic community can be exposed indefinitely without resulting in an unacceptable effect. It should be emphasized that the role of the effects analysis is to evaluate effects on covered species, and not compliance with the Clean Water Act, Basin Plans, or other regulatory guidelines. However, ecological benchmarks are provided where they are useful in evaluating effects.

Presented below is a more detailed description of the components that were examined to develop the qualitative conceptual models, and the quantitative tools that were used to more fully describe the potential effects of toxins on covered fish species. The models were developed to describe the biogeochemistry that determines how these toxins partition in the aqueous system (to sediment, water, or biota), how they are taken into the foodweb, and the potential effects on the covered fish species.

### D.4.1 Problem Formulation

Historical and current land use in the Delta has resulted in the release of potentially toxic constituents into the environment. The effects of toxic constituents on the Delta ecosystem have been identified as contributing to the POD described by Baxter (2010). Preliminary proposal actions may serve to increase or decrease the presence and effects of the toxic constituents already present in the Delta and are deserving of attention in this effects analysis.



***No comments***

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## D.4.2 Conceptual Model

Multiple chemical-specific, environmental, and species-specific factors contribute to determining whether a constituent will cause toxic effects on biota. The general conceptual model outlined below and illustrated in Figure D-1 is intended to provide a framework to evaluate these factors and a full description of the potential for each toxin to affect covered fish species under preliminary proposal actions.

The textual explanations in the following sections are meant to provide definitions of factors included in the conceptual model shown in Figure D-1 and information on how the factors work together to determine the ultimate effects on covered fish species. The conceptual model is meant to summarize and synthesize a complex system that integrates chemical-specific biogeochemistry with site-specific environmental factors and species/life stage–specific physiology.

### D.4.2.1 Conceptual Model Components—Toxin Biogeochemistry

The toxins identified in the Delta environment and the fate and transport of these chemicals, along with the propensity for these chemicals to enter the food chain, are evaluated through analysis of the factors discussed below.

#### D.4.2.1.1 Fate and Transport

The conceptual model for toxins includes a discussion of the biogeochemistry of the chemical and the fate and transport characteristics. The analysis of fate and transport involves identifying the source of the toxin in the Delta, how the constituent is transported and accumulates in the ecosystem, and the chemical properties that cause it to partition to sediment/water/air/biota. This analysis integrates the environmental setting and hydrology to determine how and where the toxin is transported from its source area to other parts of the Delta.

The basic chemical characteristics that determine how a toxin is transported and partitions in the environment include solubility in water, tendency to sorb to particulates, and volatility (tendency to occur as a vapor). A toxin with high water-solubility can migrate dissolved in rivers. Alternatively, metals and some pesticides often have low solubility in water and tend to sorb to particulates and organic carbon, so they typically are found in sediments closer to the source.

Chemicals can be broken down in the environment by chemical or biological processes. The rate of this degradation is measured by a chemical-specific half-life, which is the time it takes for half of the mass to break down. Chemical degradation includes photodegradation, where the toxin is chemically broken down by sunlight. Biological degradation is usually a product of bacterial degradation of organic chemicals.

Water chemistry also affects the fate, transport, partitioning, and bioavailability of a toxin in an aqueous system. Salinity, hardness, temperature, pH, organic carbon, and redox potential (in sediments) influence the form that a chemical will take. In many cases, certain forms of a given toxin (species or ionic state) determine partitioning and the ultimate toxicity. For example, copper is more toxic in the cupric species (2+), than in the cuprous species (1+).

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#### D.4.2.1.2 Bioavailability, Bioaccumulation

Bioavailability is a measure of the ability of a toxic to cross the cellular membrane of an organism, to become incorporated in that organism, and to enter the food chain (Semple 2004). Not all toxins are in a form that can be taken up by an organism. Bioavailability is not only chemical-specific, but it also can be specific to the chemical form that a constituent takes. For instance, copper in the 2+ state is more bioavailable than copper in the 1+ state, making the first form much more toxic than the second. Mercury in an organic complex as methylmercury is much more bioavailable and toxic than elemental mercury or mercury complexed with an inorganic compound.

In addition to the availability of the chemical to be taken up by biota, some chemicals are magnified more through the food chain. *Bioaccumulation* often is loosely used interchangeably with the term *biomagnification*. Strictly speaking, bioaccumulation occurs at any one trophic level or in any one species (and age-class) as a pollutant is ingested inside of food items or absorbed from the environment and thereby *accumulates* to some concentration in tissues of organisms at that particular trophic level or in that particular species (and age-class). In contrast, *biomagnification* more properly refers to increases in tissue concentrations of a pollutant as it passes upward through the food chain, from prey to predator, to the topmost, mature predators. In these top predators tissue concentrations may be harmful both to the animal (especially to offspring) and to those that consume it. A common example of a pollutant bioaccumulating and biomagnifying to harmful levels is the buildup of mercury in large game fish such as tuna or striped bass. In summary, bioaccumulation happens within a specific trophic level; biomagnification occurs over multiple trophic levels.

Bioaccumulation is a function of the chemical's specific characteristics and the way that the organism metabolizes the chemical—such as whether it is metabolized and excreted, or stored in fat. Toxins that are bioavailable and lipophilic (tend to accumulate in fatty tissue of an organism and are not very water soluble) typically bioaccumulate at higher rates. If stored, the chemical can biomagnify in the food chain, for example, mercury and some pesticides.

### D.4.2.2 Conceptual Model Components—Effects of Preliminary Proposal Actions on Toxins

For the purposes of this analysis, the BDCP conservation measures are grouped as either water operations or restoration, as depicted on Figure D-1. The mercury mitigation conservation measure also will be discussed within the restoration actions.

The primary concern with the BDCP habitat restoration measures regarding toxins is the potential for mobilizing toxins sequestered in sediments of the newly inundated floodplains and marshes. This appendix provides an overview of what toxins are known to be present in these areas and the biogeochemical behaviors that will determine whether they could be mobilized into the aquatic environment and the food chain by restoration actions.

The greatest potential for effects on toxins related to the preliminary proposal water operations is the potential for changes in dilution and mixing of existing toxins. For instance, certain toxins, such as selenium, are known to be present in the San Joaquin watershed. A change in the proportion of San Joaquin water inputs to the Delta relative to the Sacramento River could result in diminished dilution (and increased concentrations) in the Delta of toxins from the San Joaquin watershed. Reduction of flows in the Sacramento River downstream of north Delta intakes also may result in decreased dilution of toxins in the Delta.



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### D.4.2.3 Conceptual Model Components—Effects of Changes in Toxins on Covered Fish Species

The previous steps determine if and where preliminary proposal actions potentially could change the amounts and bioavailability of toxins. This step looks at how these changes could affect covered fish species. The toxic effects of a chemical are determined by how it works on a biochemical level. Some of the types of effects are listed in Figure D-1 under *Toxic Effects*. Toxins can target specific tissues, organs, or organ systems. For example, toxins that affect the neurological, immune, or endocrine systems typically lead to potential effects on behavior, ability to combat disease, and reproduction, respectively. Certain toxins tend to accumulate in particular tissues or organs, such as the fatty tissues, liver, or kidneys; those that accumulate in fatty tissues have a greater potential to bioaccumulate. These factors determine the overall effect of the toxin on the organism, and whether it will affect reproductive, developmental, or adult life stages. Effects of a particular toxic chemical can vary between species, and also between life stages within a species. The conceptual model for this effects analysis considers all these factors.

## D.5 Results—Effects of Preliminary Proposal Conservation Measures on Toxins

### D.5.1 Mercury

#### D.5.1.1 Mercury—Location, Environmental Fate, and Transport

Mining operations in the mountains drained by Central Valley tributaries resulted in transport and widespread deposition of mercury into the water and sediments of the Delta ecosystem. Mercury, in the form of the mineral cinnabar, was mined mainly from the Coastal Range. In the Sierra Nevada and Klamath-Trinity Mountains, mercury was used for gold recovery in placer and hard-rock mining operations (Alpers and Hunerlach 2000; Alpers et al. 2005). Inorganic mercury was transported with sediment loads by creeks and rivers draining the mountains and became distributed throughout the riverbed, marsh, wetland, and floodplain sediments of the Delta, with highest concentrations in upper tributaries.

The Sacramento River is the primary transport route of methylmercury to the Delta and contributes about 80% of riverborne mercury inputs (Stephenson 2007; Wood 2010). The amounts of methylmercury, or organic mercury, will correspond roughly with these percentages. In the Sacramento River watershed, the highest concentrations of mercury are found in Cache Creek and the Yolo Bypass where Cache Creek terminates. Cache Creek, which drains a former mining area, is the largest contributor of mercury to the Delta, as it drains 2% of the area in the Central Valley and contributes 54% of the mercury (Foe 2008). Methylmercury concentrations decrease significantly (by 30% to 60%) downstream of Rio Vista, where concentrations were at or below 0.05 nanograms per liter (ng/L) (Foe 2003; Woods 2010).

Relative to the Sacramento River, the San Joaquin River is a relatively minor contributor of methylmercury to the Delta. Methylmercury water concentrations in some waters of the San Joaquin watershed are comparable or higher than the Sacramento River, but overall loading is minor because of the low flows. The Mokelumne-Cosumnes River is the greatest contributor of mercury in the San Joaquin watershed, but accounts for only 2.1% of the total methylmercury in the Delta, with



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an average concentration of 0.17 ng/L (Woods 2010). Marsh Creek, which drains the Mt. Diablo mining area, contributes a small percentage (0.04%) because of its size, but it does have relatively high average concentrations of methylmercury estimated at 0.25 ng/L (Woods 2010). Bear Creek and Mosher Creek, which drain a former mining area, are also high in mercury, with concentrations reported at 0.31 ng/L (Woods 2010). These creeks are also small and contribute a relatively small percentage to the overall mercury budget in the Delta.

For reference, the current Criterion Continuous Concentration (AWQC-Fresh Water-Chronic) for mercury in fresh water is 770 ng/L (0.77 micrograms per liter [µg/L]). The criteria can be applied to total mercury (organic plus inorganic mercury), but they are derived from data for inorganic mercury (III) and therefore should be considered underprotective if a substantial portion of mercury occurs as methylmercury. The Delta is listed on the Clean Water Act Section 303(d) list as an impaired water body for mercury in fish tissues (State Water Resources Control Board 2011).The TMDLs for methylmercury in the Delta and in San Francisco Bay are provided in Table D-5. The TMDL for the Delta was approved recently.

**Table D-5. Mercury and Methylmercury TMDLs in the Delta and San Francisco Bay**

| Analyte | CTR[a] | EPA Recommended Criteria[b] | Delta Methylmercury TMDL[c] | San Francisco Bay Mercury TMDL[d] |
|---|---|---|---|---|
| Mercury (ng/L) | 50 | 770 | – | 25 |
| Methylmercury (ng/L) | – | – | 0.06 | – |

CTR = California Toxics Rule.
[a] Criterion for the protection of human health from total recoverable mercury in fresh water (U.S. Environmental Protection Agency 2006c).
[b] Criterion for the protection of chronic exposure from total mercury to freshwater aquatic life (U.S. Environmental Protection Agency 2006c).
[c] The recommended water column TMDL concentration of methylmercury for the protection of fish bioaccumulation (Central Valley Regional Water Quality Control Board 2011).
[d] The recommended water column 4-day average TMDL concentration for total mercury (U.S. Environmental Protection Agency 2006c).

The chemistry of mercury in the environment is complex (Figure D-2). Elemental mercury and mercury in the form of inorganic compounds have relatively low water solubility and tend to accumulate in soils and sediments. When mercury forms an organic complex called monomethylmercury (commonly referred to as methylmercury), it becomes more water soluble and the toxicity and bioavailability are greatly enhanced, making it a primary concern for ecosystem effects. The toxicity of methylmercury is amplified as it biomagnifies through the foodweb. Because of the widespread presence of toxic methylmercury in the Delta, much recent research has been completed on the cycling of methylmercury through the physical environment and biota of the area. The biogeochemistry of mercury in an aqueous system is illustrated on Figure D-2.

Conversion of inorganic mercury to methylmercury occurs in flooded fine sediments subjected to periodic drying-out periods and is associated with anaerobic (oxygen-depleted), reducing environments (Alpers et al. 2008; Ackerman and Eagles-Smith 2010). Methylmercury production is higher in high marshes that are subjected to wet and dry periods over the highest monthly tidal cycles; production appears to be lower in low marshes that are always inundated and not subject to dry periods (Alpers et al. 2008). Relatively high rates of methylmercury production also have been



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attributed to agricultural wetlands, mainly rice fields (Windham-Myers et al. 2010). Numerous other factors affect methylation of mercury in estuarine environments in addition to inundation regime; they include vegetation, grain size, pH, availability of binding constituents (iron, sulfur, organic matter), and factors influencing success of the microbes responsible for the methylation process (nutrients and dissolved oxygen) (Alpers et al. 2008; Wood et al. 2010).

In-situ production of methylmercury in Delta sediments is an important source of this toxin to the Delta ecosystem. Several investigators have quantified inputs of methylmercury to the Delta from sediments, with varying results (Stephenson 2007; Byington 2007; Foe 2008; Wood et al. 2010). Results of the CALFED Mercury Project Annual Report for 2007 (Stephenson 2007) indicate that river inputs (11.5 grams per day [g/day] methylmercury) and in-situ production from wetland/marsh sediments (11.3 g/day methylmercury) are the leading sources of methylmercury to the Delta waters, and have roughly comparable levels of input. Wood (2010) estimates that in-situ methylmercury production in open water and wetlands contributes approximately 36% of the overall methylmercury load to the Delta (approximately 5 g/day) but is less than riverine/tributary inputs (8 g/day). The higher estimate of methylmercury production from sediments reported by Stephenson is based on periods of higher water (wet) and may be more representative of what might occur when new restoration opportunity areas (ROAs) are opened for inundation, especially when combined with the effects of sea level rise.

Despite all sources of methylation, the Delta remains a net sink for waterborne methylmercury, and photodegradation that results in demethylation of mercury may be an important factor in methylmercury losses from the system (Stephenson et al. 2008).

In the methylmercury budgets developed by Woods (2010), Foe (2008), Byington (2007), and Stephenson (2007), photodegradation rates are higher than sediment production rates for methylmercury. Gill (2008) identified photodegradation of methylmercury as potentially the most effective mercury detoxification mechanism in the Delta.

Specific photodegradation rates vary on daily and monthly timescales, as the process is dependent on light intensity (Gill 2008). Photodegradation of methylmercury occurs in the photic zone of the water column (the depth of water within which natural light penetrates) and as such can be expected to occur in a large portion of the shallow, newly inundated ROAs. At the 1% light level, the mean depth for the photic zone in the Delta was calculated to be 2.6 meters, with measured depths ranging from 1.9 meters to 3.6 meters (Gill 2008; Byington 2007). Gill and Byington also conclude that photodegradation may be most active in the top half-meter of the water column in the Delta.

Mediated by sunlight, photodegradation occurs at higher levels in the dry season than in the wet season, with minimum photodegradation rates occurring December through February and maximum degradation rates occurring in May and June (Byington 2007). Research by Byington indicates that photodegradation of methylmercury in marshes and tules in the Delta is severely diminished by reduced light penetration resulting from the presence of high dissolved organic carbon (DOC), turbidity, and aquatic vegetation.

Atmospheric deposition also may contribute to the mercury load; however, estimated daily loads are an order of magnitude lower than most other sources to the Delta and constitute approximately 1% of the entire methylmercury load contributed from external and in-Delta sources (Wood et al. 2010). In addition, atmospheric contributions are not anticipated to be altered by preliminary proposal actions. Therefore, atmospheric deposition can be considered an insignificant source from the perspective of assessing preliminary proposal effects.



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### D.5.1.2 Mercury—Effects of Preliminary Proposal Conservation Measures

Quantitative modeling was performed to estimate the effects of preliminary proposal water operations on mercury and methylmercury in the aquatic system and on covered species. Modeling was based on DSM2 output that estimated changes in water flows under preliminary proposed actions. Results were considered in the context of a qualitative discussion to fully capture some of the factors that were not quantified, including mercury methylation in ROAs and biogeochemical factors that affect concentrations, environmental partitioning, degradation, and bioavailability.

#### D.5.1.2.1 Water Operations

**Modeling Methods**

Average waterborne methylmercury concentrations are compared to co-located fish tissue mercury concentrations to construct a simple regression model to predict future fish concentrations from water, as was done for the Delta methylmercury TMDL (Central Valley Regional Water Board 2011). In the case of the current study, the model is based on the DSM2-predicted blending of various source waters with known, measured average concentrations of total and methylmercury, and the known relationship between modeled methylmercury and largemouth bass fillet concentrations of mercury. The resulting model allows the prediction of future, altered average fish tissue mercury concentrations under the preliminary proposal water operations. For this modeling effort, largemouth bass was used as the example fish. Although this is not a covered fish species, there are sufficient data to develop relationships between water and fish concentrations, and largemouth bass is a high level consumer relative to the covered fish species and would show effects from bioaccumulation.

The source-water concentrations used in the model are listed in Table D-6. Modeling methods are more fully described in Attachment D.A.

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1 **Table D-6. Historical Methylmercury Concentrations in the Five Delta Source Waters for the Period 2000–2008**

| Data Parameters | Source Water | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | Sacramento River* | | San Joaquin River* | | San Francisco Bay* | | East Side Tributaries* | | Agriculture in the Delta* | |
| Mean (ng/L) | 0.10 | 0.03 | 0.15 | 0.03 | 0.032 | - | 0.22 | 0.08 | 0.25 | - |
| Minimum (ng/L) | 0.05 | 0.03 | 0.09 | 0.01 | - | - | 0.02 | 0.02 | - | - |
| Maximum (ng/L) | 0.24 | 0.03 | 0.26 | 0.08 | - | - | 0.32 | 0.41 | - | - |
| 75th Percentile (ng/L) | 0.12 | 0.03 | 0.18 | 0.06 | - | - | 0.20 | 0.15 | - | - |
| 99th Percentile (ng/L) | 0.23 | 0.03 | 0.26 | 0.08 | - | - | 0.31 | 0.39 | - | - |
| Data Source | Central Valley Water Board 2008a | | BDAT 2010; Central Valley Water Board 2008a | USGS 2010 | SFEI 2010 | - | Central Valley Water Board 2008a | USGS 2010 | Central Valley Water Board 2008a | - |
| Station(s) | Sacramento River at Freeport | | San Joaquin River at Vernalis | | Martinez | | Mokelumne and Calaveras Rivers | | Mid-Delta locations, median | |
| Date Range | 2000–2003 | 2000 | 2000–2001; 2003–2004 | 2000–2002 | 2007 | - | 2000–2001; 2003–2004 | 2000; 2002 | 2008 | - |
| ND Replaced with RL | Not Applicable | | Not Applicable | Yes | - | | Yes | | Not Applicable | |
| Data Omitted | None | | None | | - | | None | | None | |
| No. of Data Points | 36 | 1 | 49 | 25 | - | - | 27 | 9 | - | - |

Sources: BDAT Website 2010; Central Valley Regional Water Quality Control Board 2008a; San Francisco Estuary Institute Website 2010; U.S. Geological Survey Website 2010.

Notes:

Means are geometric means. ng/L = nanograms per liter.

* The total recoverable concentration of the analyte is presented in first cell and the dissolved concentration of the analyte is presented in the second column.

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- n/a -

### Modeling Results—Water Operations

Modeling showed small, insignificant changes in total mercury and methylmercury levels in water and fish tissues due to PP water operations.

Under current conditions, total mercury and methylmercury concentrations in water exceed TMDL target values, and PP water operations will not change this condition. Estimated concentrations of mercury in water under EBC2_ELT and the PP_ELT are shown in Table D-7 (for total mercury) and Table D-8 (for methylmercury). Estimated concentrations for the late-long-term (LLT) scenario are provided in Table D-10 and Table D-11.

Currently, mercury concentrations in fish tissues exceed Delta TMDL guidance targets, which are set for human health rather than effects on fish, and the PP is not expected to substantially alter this condition through water operations. Modeled concentrations of total mercury in fish are presented in Table D-9 and Table D-12.

**Table D-7. Modeled Mercury Concentrations in Water: Early Long-Term**

| Location | Period* | Period Average Concentration (µg/L) | | |
|---|---|---|---|---|
| | | Existing Conditions (EBC2) | EBC2_ELT | PP_ELT |
| **Delta Interior** | | | | |
| Mokelumne River at Staten Island | All | 0.0052 | 0.0052 | 0.0054 |
| | Drought | 0.0046 | 0.0047 | 0.0048 |
| San Joaquin River at Buckley Cove | All | 0.0075 | 0.0076 | 0.0075 |
| | Drought | 0.0073 | 0.0075 | 0.0074 |
| Old River at Rancho del Rio | All | 0.0051 | 0.0051 | 0.0052 |
| | Drought | 0.0046 | 0.0046 | 0.0045 |
| **Western Delta** | | | | |
| Sacramento River above Pt. Sacramento | All | 0.0044 | 0.0044 | 0.0045 |
| | Drought | 0.0044 | 0.0045 | 0.0045 |
| San Joaquin River at Antioch Ship Channel | All | 0.0050 | 0.0051 | 0.0052 |
| | Drought | 0.0049 | 0.0050 | 0.0049 |
| Sacramento River at Mallard Island | All | 0.0056 | 0.0056 | 0.0058 |
| | Drought | 0.0058 | 0.0059 | 0.0059 |
| | Drought | 0.0058 | 0.0060 | 0.0057 |

Notes:
The recommended water column 4-day average TMDL concentration for total mercury = 0.025 µg/L. (U.S. Environmental Protection Agency 2006c.)
* All: Water years 1975–1991 represent the 16-year period modeled using DSM2. Drought: Represents a 5-consecutive year (water years 1987–1991) drought period consisting of drought and critical water-year types (as defined by the Sacramento Valley 40-30-30 water year hydrologic classification index).
These data are preliminary and are subject to change as BDCP analyses are finalized.



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## No comments

- n/a -

**Table D-8. Modeled Methylmercury Concentrations in Water: Early Long-Term**

| Location | Period* | Period Average Concentration (µg/L) | | |
|---|---|---|---|---|
| | | Existing Conditions (EBC2) | EBC2_ELT | PP_ELT |
| Delta Interior | | | | |
| Mokelumne River at Staten Island | All | *0.000136* | *0.000135* | *0.000145* |
| | Drought | *0.000122* | *0.000122* | *0.000127* |
| San Joaquin River at Buckley Cove | All | *0.000159* | *0.000164* | *0.000166* |
| | Drought | *0.000161* | *0.000168* | *0.000172* |
| Old River at Rancho del Rio | All | *0.000122* | *0.000122* | *0.000124* |
| | Drought | *0.000113* | *0.000114* | *0.000115* |
| Western Delta | | | | |
| Sacramento River above Pt. Sacramento | All | *0.000103* | *0.000103* | *0.000104* |
| | Drought | *0.000101* | *0.000101* | *0.000101* |
| San Joaquin River at Antioch Ship Channel | All | *0.000104* | *0.000103* | *0.000105* |
| | Drought | *0.000094* | *0.000093* | *0.000094* |
| Sacramento River at Mallard Island | All | *0.000083* | *0.000083* | *0.000083* |
| | Drought | *0.000073* | *0.000072* | *0.000072* |
| | Drought | *0.000135* | *0.000136* | *0.000133* |

Notes:
The recommended water column TMDL concentration of methylmercury for the protection of fish bioaccumulation = 0.06 ng/L (.00006 µg/L). (Central Valley Regional Water Quality Control Board 2008a.) Exceedances are shaded and in italics.
* All: Water years 1975–1991 represent the 16-year period modeled using DSM2. Drought: Represents a 5-consecutive year (water years 1987–1991) drought period consisting of drought and critical water-year types (as defined by the Sacramento Valley 40-30-30 water year hydrologic classification index).
These data are preliminary and are subject to change as BDCP analyses are finalized.

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## *No comments*

- n/a -

**Table D-9. Modeled Mercury Concentrations in Largemouth Bass Fillets: Early Long-Term**

| Location | Period* | ELT Period Average Largemouth Bass Fillet Mercury Concentrations (mg/kg ww) | | |
|---|---|---|---|---|
| | | Existing Conditions (EBC2) | EBC2_ELT | PP_ELT |
| **Delta Interior** | | | | |
| Mokelumne River at Staten Island | All | *0.521* | *0.516* | *0.561* |
| | Drought | *0.459* | *0.459* | *0.481* |
| San Joaquin River at Buckley Cove | All | *0.624* | *0.647* | *0.656* |
| | Drought | *0.633* | *0.666* | *0.684* |
| Old River at Rancho del Rio | All | *0.459* | *0.459* | *0.467* |
| | Drought | *0.420* | *0.424* | *0.428* |
| Western Delta | | | | |
| Sacramento River above Pt. Sacramento | All | *0.377* | *0.377* | *0.381* |
| | Drought | *0.368* | *0.368* | *0.368* |
| San Joaquin River at Antioch Ship Channel | All | *0.381* | *0.377* | *0.385* |
| | Drought | *0.339* | *0.334* | *0.339* |
| Sacramento River at Mallard Island | All | *0.293* | *0.293* | *0.293* |
| | Drought | *0.252* | *0.248* | *0.248* |

Notes:
Fish tissue concentrations were evaluated in relation to the Delta methylmercury TMDL tissue targets of 0.24 mg mercury/kg wet-weight of largemouth bass fillets (muscle tissue) for fish normalized to a standard 350 mm total length (Central Valley Regional Water Quality Control Board 2008a). Exceedances are shaded and in italics.
* All: Water years 1975–1991 represent the 16-year period modeled using DSM2. Drought: Represents a 5-consecutive year (water years 1987–1991) drought period consisting of drought and critical water-year types (as defined by the Sacramento Valley 40-30-30 water year hydrologic classification index).
These data are preliminary and are subject to change as BDCP analyses are finalized.

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## *No comments*

- n/a -

1 **Table D-10. Modeled Mercury Concentrations in Water: Late Long-Term**

| Location | Period* | Period Average Concentration (µg/L) | | |
|---|---|---|---|---|
| | | Existing Conditions (EBC) | EBC2_LLT | PP_LLT |
| **Delta Interior** | | | | |
| Mokelumne River at Staten Island | All | *0.0052* | *0.0051* | *0.0053* |
| | Drought | *0.0046* | *0.0046* | *0.0047* |
| San Joaquin River at Buckley Cove | All | *0.0075* | *0.0075* | *0.0075* |
| | Drought | *0.0073* | *0.0073* | *0.0074* |
| Old River at Rancho del Rio | All | *0.0051* | *0.0051* | *0.0053* |
| | Drought | *0.0046* | *0.0046* | *0.0047* |
| **Western Delta** | | | | |
| Sacramento River above Pt. Sacramento | All | *0.0044* | *0.0045* | *0.0045* |
| | Drought | *0.0044* | *0.0045* | *0.0045* |
| San Joaquin River at Antioch Ship Channel | All | *0.0050* | *0.0050* | *0.0052* |
| | Drought | *0.0049* | *0.0049* | *0.0049* |
| Sacramento River at Mallard Island | All | *0.0056* | *0.0056* | *0.0058* |
| | Drought | *0.0058* | *0.0059* | *0.0059* |
| | Drought | *0.0058* | *0.0060* | *0.0058* |

Notes:
The recommended water column 4-day average TMDL concentration for total mercury = 0.025 µg/L. (U.S. Environmental Protection Agency 2006c.) Exceedances are shaded and in italics.
* All: Water years 1975–1991 represent the 16-year period modeled using DSM2. Drought: Represents a 5-consecutive year (water years 1987–1991) drought period consisting of drought and critical water-year types (as defined by the Sacramento Valley 40-30-30 water year hydrologic classification index).
These data are preliminary and are subject to change as BDCP analyses are finalized.

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## *No comments*

- n/a -

**Table D-11. Modeled Methylmercury Concentrations in Water: Late Long-Term**

| Location | Period* | Period Average Concentration (µg/L) | | |
|---|---|---|---|---|
| | | EBC | EBC2_LLT | PP_LLT |
| **Delta Interior** | | | | |
| Mokelumne River at Staten Island | All | *0.000136* | *0.000134* | *0.000142* |
| | Drought | *0.000122* | *0.000121* | *0.000126* |
| San Joaquin River at Buckley Cove | All | *0.000159* | *0.000164* | *0.000162* |
| | Drought | *0.000161* | *0.000168* | *0.000167* |
| Old River at Rancho del Rio | All | *0.000122* | *0.000123* | *0.000126* |
| | Drought | *0.000113* | *0.000116* | *0.000118* |
| **Western Delta** | | | | |
| Sacramento River above Pt. Sacramento | All | *0.000103* | *0.000103* | *0.000103* |
| | Drought | *0.000101* | *0.000101* | *0.000100* |
| San Joaquin River at Antioch Ship Channel | All | *0.000104* | *0.000103* | *0.000105* |
| | Drought | *0.000094* | *0.000094* | *0.000094* |
| Sacramento River at Mallard Island | All | *0.000083* | *0.000083* | *0.000082* |
| | Drought | *0.000073* | *0.000073* | *0.000072* |
| | Drought | *0.000135* | *0.000138* | *0.000136* |

Notes:
The recommended water column TMDL concentration of methylmercury for the protection of fish bioaccumulation = 0.06 ng/L (0.00006 µg/L). (Central Valley Regional Water Quality Control Board 2008a.)
Exceedances are shaded an in italics.
* All: Water years 1975–1991 represent the 16-year period modeled using DSM2. Drought: Represents a 5-consecutive year (water years 1987–1991) drought period consisting of drought and critical water-year types (as defined by the Sacramento Valley 40-30-30 water year hydrologic classification index).
These data are preliminary and are subject to change as BDCP analyses are finalized.

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## *No comments*

- n/a -

**Table D-12. Modeled Mercury Concentrations in Largemouth Bass Fillets: Late Long-Term**

| Location | Period* | LLT Period Average Largemouth Bass Fillet Mercury Concentration (mg/kg ww) | | |
|---|---|---|---|---|
| | | EBC | EBC2_LLT | PP_LLT |
| **Delta Interior** | | | | |
| Mokelumne River at Staten Island | All | *0.521* | *0.512* | *0.547* |
| | Drought | *0.459* | *0.454* | *0.476* |
| San Joaquin River at Buckley Cove | All | *0.624* | *0.647* | *0.638* |
| | Drought | *0.633* | *0.666* | *0.661* |
| Old River at Rancho del Rio | All | *0.459* | *0.463* | *0.476* |
| | Drought | *0.420* | *0.433* | *0.441* |
| **Western Delta** | | | | |
| Sacramento River above Pt. Sacramento | All | *0.377* | *0.377* | *0.377* |
| | Drought | *0.368* | *0.368* | *0.364* |
| San Joaquin River at Antioch Ship Channel | All | *0.381* | *0.377* | *0.385* |
| | Drought | *0.339* | *0.339* | *0.339* |
| Sacramento River at Mallard Island | All | *0.293* | *0.293* | *0.289* |
| | Drought | *0.252* | *0.252* | *0.248* |

Notes:
Fish tissue concentrations were evaluated in relation to the Delta methylmercury TMDL tissue targets of 0.24 mg mercury/kg wet-weight of largemouth bass fillets (muscle tissue) for fish normalized to a standard 350 mm total length (Central Valley Regional Water Quality Control Board 2008a). Exceedances are shaded an in italics.
* All: Water years 1975–1991 represent the 16-year period modeled using DSM2. Drought: Represents a 5–consecutive year (water years 1987–1991) drought period consisting of drought and critical water-year types (as defined by the Sacramento Valley 40-30-30 water year hydrologic classification index).
These data are preliminary and are subject to change as BDCP analyses are finalized.

**Uncertainty Analysis**

The model captures effects due to preliminary proposal water operations but does not estimate the potential for methylation in existing or newly created environments (e.g., ROAs). The detailed, site-specific information needed to construct such a model, with acceptable margins of error, is lacking but may be developed as part of specific, future evaluations of actions (see discussion above concerning key processes controlling mercury fate, transport, and risk determination). Agricultural and existing wetlands may be very different in production of methylmercury and uptake into various trophic levels and are not easily generalized or modeled (Windham-Myers et al. 2010).

### D.5.1.2.2 Restoration

As discussed above, in-situ conversion of mercury to methylmercury occurs at highest rates in intermittently flooded marshes and floodplains, as well as flooded agricultural areas. Preliminary proposal restoration actions will expand intermittently wetted areas by converting managed marshes, diked wetlands, agricultural areas, and other upland areas to tidal, open-water, and floodplain habitats (see Chapter 3, *Conservation Strategy*, for details of restoration), resulting in new areas with the potential to increase methylmercury in the aquatic system.



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## *No comments*

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Woods and coauthors (2010) estimated rates of methylmercury generation for intertidal and floodplain areas (0.0369 g/acre/year) and for open-water production (0.01476 g/acre/year). However, methylmercury generation rates ultimately are dependent on the concentrations of mercury in the soils and on the specific biogeochemistry of the system. For this effects analysis, the margin of error on applying these estimated production rates across a wide geographic area with varying hydrology and concentrations of sequestered mercury was deemed to be too large to produce a reliable estimate of methylmercury generation at the scale of the ROAs.

The Sacramento River watershed, and specifically the Yolo Bypass, is the primary source of mercury in the Delta. The highest concentrations of mercury and methylmercury are in the Cache Creek area and the Yolo Bypass. The amount of methylmercury produced in the Yolo Bypass has been estimated to represent 40% of the total methylmercury production for the entire Sacramento watershed (Foe et al. 2008). Water discharging from the Yolo Bypass at Prospect Slough has a reported average annual methylmercury concentration of 0.27 ng/L, compared to the 0.06 ng/L TMDL (set for human health from bioaccumulation effects in fish).

The highest levels of methylmercury generation, mobilization, and bioavailability are expected in the Yolo Bypass, which will be subjected to more frequent and wider areas of inundation under the preliminary proposal actions. The concentrations of methylmercury in water exiting the Yolo Bypass will depend on many variables. Recent studies in the Yolo Wildlife Management Area showed that methylmercury increased with increased flow rates and increased residence time (Windham-Myer 2010). This same study also noted that the residence time in Cache Settling Basin, seasonality, and agricultural practices all factor into methylmercury production and cycling through the system in the Yolo Bypass. Marvin-DiPasquale and coauthors (2009) also identified a wide range of site-specific factors that determine methylmercury production, as well as variability in distribution and speciation of mercury in wetlands in the Yolo Bypass. Foe and coauthors (2008) developed an empirical relationship between net methylmercury production in the Yolo Bypass and outflow (methylmercury production = $0.0042*(\text{flow})^{0.782}$), but given the varied factors controlling methylmercury cycling, this calculation will not provide an estimate of methylmercury production in the Yolo Bypass that can be relied on with any certainty.

The preliminary proposal for the Yolo Bypass has the potential to increase the loading, concentrations, and bioavailability of methylmercury in the aquatic system in the Yolo Bypass. Currently, the methylmercury in water discharging from the Yolo Bypass to the Sacramento River is 0.27 ng/L (annual average) (Foe et al. 2008). This concentration likely will increase under the preliminary proposal, but will be mitigated to some extent by CM12, as discussed below. The current and future concentrations of methylmercury will exceed the TMDL (set for human health from bioaccumulation effects in fish) concentration of 0.06 ng/L. Also, decreased flows in the Sacramento River due to preliminary proposal upstream water operations may reduce the dilution capacity of the Sacramento River and result in increased concentrations of methylmercury in the river.

As part of the preliminary proposal, measures will be implemented to mitigate the production of methylmercury in ROAs. These measures may include construction and grading that minimize exposure of mercury-containing soils to the water column, design to support photodegradation, and pre-design field studies to identify depositional areas where mercury accumulation is most likely and characterization and/or design that avoids these areas. Recent studies performed by Heim with others (in press) indicate that integrating permanent ponds into restoration designs may reduce mercury methylation and mobilization. CM12 provides for consideration of new information as it develops that could effectively minimize methylmercury production and mobilization. Also, the



## *No comments*

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Delta TMDL for methylmercury was adopted recently (Central Valley Regional Water Quality Control Board 2011) and will be integrated into the overall preliminary proposal through CM12 (discussed below) and adaptive management.

Photodegradation may be an important factor in reducing methylmercury generation, and design to enhance photodegradation has been included in CM12. Recent research has indicated that photodegradation of methylmercury in shallow waters can remove an amount of methylmercury similar to that produced in sediments of the Delta system (Byington 2008). Photodegradation has high potential to remove a percentage of the methylmercury produced in newly restored areas, with the rates partially dependent on the turbidity of the water column and the resultant depth of the photic zone. However, demethylation by photodegradation still leaves the less toxic inorganic mercury in the system. More research into the fate of mercury following photodegradation is needed.

As discussed throughout this section, the biogeochemistry and fate and transport of mercury and methylmercury are very complex. Restoration will involve inundation of areas where mercury has been sequestered in soils, and if methylation occurs, the methylmercury will be mobilized into the aquatic system. Once in the aquatic system, the methylmercury can be transported with water flow, taken up by biota, volatilized, demethylated, and returned to sediment (but not necessarily at the original restoration site). As a result of these processes, the mercury may be transported away from the restoration site, resulting in an overall decrease of mercury in the soils, which will reduce the source at the ROA. Based on this conceptual model, the mercury available for methylation at the ROA may decrease over time. However, the length of time for this to be quantifiable is not known.

#### D.5.1.2.3 Mercury Summary

Preliminary proposal restoration actions are likely to result in increased production, mobilization, and bioavailability of methylmercury in the aquatic system. Modeling of water operations effects showed little changes in methylmercury concentrations in water or fish tissue, although methylmercury concentrations in both media would continue to exceed criteria under the preliminary proposal.

Methylmercury likely would be generated by inundation of restoration areas, with highest concentrations expected in the Yolo Bypass, Cosumnes and Mokelumne Rivers, and at other ROAs closest to these source areas.

CM12 Methylmercury Management will help to minimize the increased mobilization of methylmercury at restoration areas. It describes pre-design characterization, design elements, and best management practices to mitigate methylation of mercury, and requires monitoring and reporting of observed methylmercury levels.

## D.5.2 Selenium

### D.5.2.1 Selenium—Location, Environmental Fate, and Transport

Selenium is a naturally occurring micronutrient that can have significant ecological effects at elevated concentrations. Selenium has been identified as an important toxin in the Delta, especially in the San Joaquin watershed where irrigation practices mobilize naturally occurring selenium from the soils. In the Delta watershed, selenium is most enriched in marine sedimentary rocks of the Coast Ranges on the western side of the San Joaquin Valley (Presser and Piper 1998). Irrigation of

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***No comments***

- n/a -

soils derived from the marine rocks leaches the selenium, and the subsequent practice by farmers to drain excess shallow groundwater from the root zone to protect their crops results in elevated concentrations of selenium in groundwater and receiving rivers (McCarthy and Grober 2001).

For reference, the current AWQC-Fresh Water-Chronic for selenium in fresh water is 5.0 µg/L and is expressed as the total recoverable metal in the water column. In the Grassland waterways and Salt Slough, a more protective chronic value of 2 µg/L applies, in consideration of sensitive listed species. The lentic conditions of water in the marshes were also a factor in setting these site-specific objectives. Available criteria, standards, and objectives for selenium are presented in Table D-13.

**Table D-13. Applicable Federal Criteria, State Standards/Objectives, and Other Relevant Effect Thresholds for Selenium**

| | Region 5 Basin Plan[a] | Region 2 Basin Plan[b] | CTR[c] | Drinking Water MCL[d] | EPA Recommended Criteria[e] | Other Relevant Thresholds[f] |
|---|---|---|---|---|---|---|
| Selenium (µg/L) | 5/12 | 5/20 | 5/20 | 50 | 5/variable | 2 |

[a] Objectives apply to the lower San Joaquin River from the mouth of the Merced River to Vernalis as 5 µg/L (4-day average) and 12 µg/L (maximum concentration) total selenium concentration (Central Valley Regional Water Quality Control Board 2009a).

[b] Selenium criteria were promulgated as total recoverable concentrations for all San Francisco Bay/Delta waters in the National Toxics Rule (NTR) (U.S. Environmental Protection Agency 1992; San Francisco Bay Regional Water Quality Control Board 2007).

[c] Standard is Criterion Continuous Concentration as 5 µg/L total recoverable selenium; California Toxics Rule (CTR) deferred to the NTR for San Francisco Bay/Delta waters and San Joaquin River (U.S. Environmental Protection Agency 2000).

[d] In addition, the California Office of Environmental Health Hazard Assessment (2010) has recommended a Public Health Goal of 30 µg/L.

[e] Criteria for protection of freshwater aquatic life are 5 µg/L (continuous concentration, 4-day average) total recoverable selenium and they vary for the Criterion Maximum Concentration (CMC) (24-hour average) (U.S. Environmental Protection Agency 2010). The CMC = 1/[(f1/CMC1) + (f2/CMC2)] where f1 and f2 are the fractions of total selenium that are treated as selenite and selenate, respectively.

[f] Concentration as total recoverable selenium identified as a Level of Concern for the Grassland Bypass Project (Beckon et al. 2008) and the site-specific objective for the Grassland (Central Valley Regional Water Quality Control Board 1996).

It should be noted that in addition to the adopted water quality objectives shown here, at the national level, EPA plans to propose Clean Water Act Section 304(a) selenium guidance criteria for aquatic life for freshwater chronic values only, and will distinguish between flowing and standing waters (U.S. Environmental Protection Agency 2011). These guidance criteria will form the basis for adopting protective water quality standards expressed as tissue concentration of selenium in fish egg or ovary and a corresponding water column concentration, where tissue concentration data are not available. Concentrations in tissue, such as bird eggs or fish tissue, better indicate actual exposure and, in combination with foodweb information, provide a basis for deriving site-specific numeric water column values. The revised national guidance criteria will be supplemented by regional efforts. EPA Region 9, in conjunction with the U.S. Geological Survey (USGS), U.S. Fish and Wildlife Service (USFWS), and National Marine Fisheries Service (NMFS) and pursuant to its obligations under the Endangered Species Act, is developing criteria to protect threatened and endangered wildlife species, aquatic-dependent species, and aquatic life in California. The first phase of this effort addresses San Francisco Bay and the Delta. It uses data on affected species and relies on



## *No comments*

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the Presser-Luoma (2010) ecosystem-based model, a model that accounts for foodweb processes and site-specific conditions. This phase is scheduled for completion in 2011, followed by a second phase for statewide criteria (including the San Joaquin River and its tributaries).

Selenium is highly bioaccumulative and can cause chronic toxicity (especially impaired reproduction) in fish and aquatic birds (Ohlendorf 2003; San Francisco Bay Regional Water Quality Control Board 2009). Developmental effects on fish from selenium are well-documented; locally, significant ecosystem effects were described in the early 1980s from water management practices that discharged groundwater containing selenium to the Kesterson Reservoir in the San Joaquin Valley, California. The fate and transport section below provides an overview of selenium sources in the Delta, and the biogeochemical processes that result in increased bioavailability of selenium in an aqueous system. The discussion focuses on the San Joaquin watershed and how selenium could be mobilized by preliminary proposal actions.

The main controllable sources of selenium in the Bay-Delta estuary are agricultural drainage (generated by irrigation of seleniferous soils in the western side of the San Joaquin basin) and discharges from North Bay refineries (in processing selenium-rich crude oil). Both the San Joaquin River and North Bay selenium loads have declined in the last 15 years in response to, first, a control program in the San Joaquin Grassland area, and, second, National Pollutant Discharge Elimination System (NPDES) permit requirements established for refineries in the late 1990s. The annual loads of selenium (mostly as selenate) entering the Bay-Delta estuary from the San Joaquin and Sacramento Rivers vary by water year (that is, by flow), but dissolved selenium loadings averaged 2,380 kg/year from the San Joaquin and 1,630 kg/year from the Sacramento in the 1990–2007 period. The Sacramento River selenium concentration, however, is essentially at background levels (.06 +/-.02 µ/L), without evidence of significant controllable sources (U.S. Environmental Protection Agency 2011).

The San Joaquin watershed, and specifically the Grassland section of the watershed, historically has been identified as a source of selenium to the Delta. However, mitigation measures have been put into place to manage selenium discharges to meet regulatory requirements. According to the Grassland Project Report for 2006–2007, selenium loads already had been reduced by 75% in 2007 relative to 1996 levels (San Francisco Estuary Institute for the Oversight of the Grassland Project Subcommittee—Chapter 2, 2006–2007). Concentrations of selenium in Salt Slough reportedly met the monthly mean goal of 2 µg/L (U.S. Environmental Protection Agency 2011b). Selenium concentrations measured in the San Joaquin River were consistently below 5 µg/L (San Francisco Estuary Institute for the Oversight of the Grassland Project Subcommittee—Chapter 2, 2006–2007). As selenium discharge from the Grassland continues to decrease as the 5 µg/L goal is approached, concentrations in the San Joaquin River also can be expected to decrease.

Under the Grassland Bypass Project, selenium discharges to Mud Slough (in the San Joaquin watershed) must be reduced to 5 µg/L (4-day average) by December 31, 2019. Further, the Central Valley Regional Water Quality Control Board (2010a) recently approved an amendment to the basin plan in light of this project. The amendment requires that agricultural drainage be halted after December 31, 2019, unless water quality objectives are met in Mud Slough (north) and the San Joaquin River between Mud Slough (north) and the mouth of the Merced River. Also, if the State Water Resources Control Board (State Water Board) finds that timely and adequate mitigation is not being implemented, it can prohibit discharge any time before December 31, 2019. As a result, a substantial reduction in selenium inputs (unrelated to the preliminary proposal) to the San Joaquin



## *No comments*

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River by 2019 would be expected to result in lower selenium inputs to the Delta from the San Joaquin River.

Elevated selenium concentrations also have been identified in Suisun Bay. Although particulate concentrations of selenium (the most bioavailable) in this region are considered low, typically between 0.5 and 1.5 micrograms per gram (µg/g), the bivalve *C. amurensis* contains elevated levels of selenium that range from 5 to 20 µg/g (Stewart 2004). Given the fact that *C. amurensis* may occur in abundances of up to 50,000 per $m^2$, this area can be considered a sink for selenium because 95% of the biota in some areas are made up of this clam.

Selenium can occur in four oxidation stages as selenates ($Se^{6+}$), selenites ($Se^{4+}$), selenides ($Se^{2-}$), and elemental selenium. The oxidized state, selenates ($Se^{6+}$), is soluble and the predominant species in alkaline surface waters and oxidizing soil conditions. Selenates are readily reduced to selenites ($Se^{4+}$) and selenides ($Se^{2-}$), which are more bioavailable than selenate. Further reduction to elemental selenium can result in an insoluble precipitate, which is not bioavailable.

Although selenium is soluble in an oxidized state, the majority typically becomes reduced and partitions into the sediment/particulate phases in an aqueous system; these reduced sediment/particulate phases are the most bioavailable (Presser and Luoma 2010). Selenium in soils is taken up by plant roots and microbes and enters the food chain through uptake by lower organisms. A portion of the selenium also is recycled into sediments as biological detritus. Lemly and Smith (1987) indicate that up to 90% of the total selenium in an aquatic system may be in the upper few centimeters of sediment and overlying detritus (Lemly 1998).

Oxidized forms of selenium (selenates and selenites) may reduce further to precipitate as elemental selenium or complex with particulates. Selenate reduces to elemental selenium through dissimilatory reduction through reactions with bacteria. These reactions reduce selenium from surface waters, resulting in an increase in selenium concentrations in sediment over time. In wetlands in particular, the organic-rich stagnant waters create a chemically reducing environment in which dissolved selenate is able to convert to selenite or elemental selenium (Werner et al. 2008). The longer the residence time of surface waters, the higher the particulate concentration resulting in higher selenium concentrations in wetlands and shallows (Presser and Luoma 2006). Aquatic systems in shallow, slow-moving water with low flushing rates are thought to accumulate selenium most efficiently (Presser and Luoma 2006; Lemly 1998). However, the ratio of selenium in particulates (which is more bioavailable) to selenium in the water column is a complex relationship that can vary across different hydrologic regimes and seasons (Presser and Luoma 2010).

Because bioaccumulation can be an important component of selenium toxicity, water column selenium concentrations are not reliable indicators of risk to biota (Presser and Luoma 2010). Selenium enters the food chain at a low trophic level and, under certain conditions, is magnified up the food chain. Lower trophic organisms can bioaccumulate hundreds of times the waterborne concentration of selenium, especially where a food chain is based on sessile filter feeders. However, research has demonstrated that bioaccumulation is less important when the food chain is based on plankton rather than on sessile filter feeders, because plankton excrete most of the selenium they consume (Stewart 2004). This is an important factor that mitigates bioaccumulation in some of the preliminary proposal covered fish species, and is more fully discussed in later sections of this appendix.



## *No comments*

- n/a -

### D.5.2.2 Selenium—Effects of Preliminary Proposal Conservation Measures

Because the San Joaquin River historically has been a major contributor of selenium to the Delta system, there is concern that the increased contribution to the Delta from the San Joaquin River relative to the Sacramento River as a result of preliminary proposal operations would result in an increase in selenium transport and bioaccumulation in the Delta.

Quantitative modeling was performed to estimate the effects of preliminary proposal water operations on selenium in the aquatic system and on covered fish species. Modeling was based on DSM2 output that estimated changes in water flows under the preliminary proposed actions, and estimated selenium concentrations in source waters that discharge into the Delta. Results were considered in the context of a qualitative discussion to fully capture some of the factors that were not quantified.

#### D.5.2.2.1 Water Operations

**Modeling Methods**

Quantitative models were used to estimate the concentrations of selenium in the water column and expected resultant concentrations of selenium in fish tissue. Modeling methods for estimating selenium concentrations in water and in fish tissue for EBC, EBC2_ELT/LLT and PP_ELT/LLT are described in Attachment D.B to this appendix. The modeling is based on water and fish tissue sample data and DSM2 model results, and provides an analysis of the effects of preliminary proposal water operations on selenium concentrations.

The output from the DSM2 model (expressed as percent inflow from different sources) was used in combination with the available measured waterborne selenium concentrations to model concentrations of selenium at locations throughout the Delta. These modeled waterborne selenium concentrations were used in the relationship model to estimate bioaccumulation of selenium in whole-body fish and bird eggs. Selenium concentrations in fish fillets then were estimated from those in whole-body fish.

Selenium concentrations in whole-body fish and bird eggs were calculated using ecosystem-scale models developed by Presser and Luoma (2010). The models were developed using biogeochemical and physiological factors from laboratory and field studies; information on loading, speciation, and transformation to particulate material; bioavailability; bioaccumulation in invertebrates; and trophic transfer to predators. Important components of the methods included (1) empirically determined environmental partitioning factors between water and particulate material that quantify the effects of dissolved speciation and phase transformation; (2) concentrations of selenium in living and non-living particulates at the base of the foodweb that determine selenium bioavailability to invertebrates; and (3) selenium biodynamic foodweb transfer factors that quantify the physiological potential for bioaccumulation from particulate matter to consumer organisms and prey to their predators.

For this modeling effort, largemouth bass was used as the example fish. Although this is not a covered fish species, there are sufficient data to develop relationships between water and fish concentrations, and largemouth bass is a voracious consumer—a high level consumer relative to the covered fish species—and would show effects of bioaccumulation.



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## *No comments*

- n/a -

The source-water concentrations used in the model are listed in Table D-14. Modeling methods are described more fully in Attachment D.B.

**Table D-14. Historical Selenium Concentrations in the Five Delta Source Waters for the Period 1996–2010**

| Source Water | Sacramento River[a] | San Joaquin River[b] | San Francisco Bay[a] | East Side Tributaries[c] | Agriculture in the Delta[a] |
|---|---|---|---|---|---|
| Mean (µg/L)[d] | 0.32 | 0.84 | 0.09 | 0.1 | 0.11 |
| Minimum (µg/L) | 0.04 | 0.40 | 0.03 | 0.1 | 0.11 |
| Maximum (µg/L) | 1.00 | 2.80 | 0.45 | 0.1 | 0.11 |
| 75th percentile (µg/L) | 1.00 | 1.20 | 0.11 | 0.1 | 0.11 |
| 99th percentile (µg/L) | 1.00 | 2.60 | 0.41 | 0.1 | 0.11 |
| Data Source | USGS Website 2010 | SWAMP Website 2009 | SFEI Website 2010 | None | Lucas and Stewart 2007 |
| Station(s) | Sacramento River at Freeport | San Joaquin River at Vernalis (Airport Way) | Central-West; San Joaquin River near Mallard Is. (BG30) | None | Mildred Island, Center |
| Date Range | 1996–2001, 2007–2010 | 1999–2007 | 2000–2008 | None | 2000, 2003–2004 |
| ND Replaced with RL | Yes | Yes | Yes | Not applicable | No |
| Data Omitted | None | Pending Data | None | Not applicable | No |
| No. of Data Points | 62 | 453 | 11 | None | 1 |

Sources: U.S. Geological Survey Website 2010; SWAMP Website 2009; San Francisco Estuary Institute Website 2010; Lucas and Stewart 2007.

[a] Dissolved selenium concentration.

[b] Not specified whether total or dissolved selenium.

[c] Dissolved selenium concentration in Mokelumne, Calaveras, and Cosumnes Rivers is assumed to be 0.1 µg/L because of lack of available data and lack of sources that would be expected to result in concentrations greater than 0.1 µg/L.

[d] Means are geometric means.

### D.5.2.2.2 Modeling Results—Selenium

Note to reviewers: these modeling results will be finalized in the EIR/EIS. The information below is preliminary and subject to update.

Selenium concentrations in the water column for the EBC2_ELT/LLT, and for the preliminary proposal (PP_ELT and PP_LLT) are listed in Table D-15 and Table D-16. These tables also provide estimates for drought years only, when there is potential for greater effects. Generally, concentrations for both the early and late long-term were slightly lower for the preliminary proposal scenarios than the existing conditions. None of the resultant water concentrations of selenium exceeded 2 µg/L, which is considered protective of fish species and is the lowest identified benchmark for selenium in water (see Table D-15 and Table D-16).

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## *No comments*

- n/a -

**Table D-15. Modeled Selenium Concentrations in Water for Early Long-Term**

| Location | Period* | Period Average Concentration (µg/L) | | |
|---|---|---|---|---|
| | | EBC | EBC2_ELT | PP_ELT |
| **Delta Interior** | | | | |
| Mokelumne River (SF) at Staten Island | All | 0.260 | 0.261 | 0.247 |
| | Drought | 0.286 | 0.285 | 0.278 |
| San Joaquin River at Buckley Cove | All | 0.756 | 0.710 | 0.673 |
| | Drought | 0.721 | 0.649 | 0.595 |
| Old River at Rancho del Rio | All | 0.393 | 0.389 | 0.411 |
| | Drought | 0.315 | 0.313 | 0.304 |
| **Western Delta** | | | | |
| Sacramento River above Pt. Sacramento | All | 0.312 | 0.311 | 0.312 |
| | Drought | 0.299 | 0.297 | 0.295 |
| San Joaquin River at Antioch Ship Channel | All | 0.312 | 0.310 | 0.324 |
| | Drought | 0.273 | 0.270 | 0.268 |
| Sacramento River at Mallard Island | All | 0.252 | 0.251 | 0.254 |
| | Drought | 0.213 | 0.210 | 0.209 |
| | Drought | 0.511 | 0.512 | 0.484 |

Notes:
µg/L = microgram(s) per liter.
Results compared to lowest of relevant thresholds—Level of Concern for the Grassland Bypass Project = 2 µg/L. (Beckon et al. 2008.) Exceedances would be shaded and in italics—there are no exceedances.
* All: Water years 1975–1991 represent the 16-year period modeled using DSM2. Drought: Represents a 5-consecutive year (water years 1987–1991) drought period consisting of dry and critical water-year types (as defined by the Sacramento Valley 40-30-30 water year hydrologic classification index).
These data are preliminary and are subject to change as BDCP analyses are finalized.

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## *No comments*

- n/a -

**Table D-16. Modeled Selenium Concentrations in Water for Late Long-Term**

| Location | Period* | Period Average Concentration (µg/L) | | |
|---|---|---|---|---|
| | | Existing Conditions | EBC2_LLT | PP_LLT |
| **Delta Interior** | | | | |
| Mokelumne River (SF) at Staten Island | All | 0.260 | 0.263 | 0.251 |
| | Drought | 0.286 | 0.287 | 0.279 |
| San Joaquin River at Buckley Cove | All | 0.756 | 0.693 | 0.700 |
| | Drought | 0.721 | 0.623 | 0.643 |
| Old River at Rancho del Rio | All | 0.393 | 0.388 | 0.411 |
| | Drought | 0.315 | 0.319 | 0.311 |
| **Western Delta** | | | | |
| Sacramento River above Pt. Sacramento | All | 0.312 | 0.312 | 0.310 |
| | Drought | 0.299 | 0.297 | 0.295 |
| San Joaquin River at Antioch Ship Channel | All | 0.312 | 0.309 | 0.323 |
| | Drought | 0.273 | 0.272 | 0.270 |
| Sacramento River at Mallard Island | All | 0.252 | 0.251 | 0.250 |
| | Drought | 0.213 | 0.212 | 0.208 |
| | Drought | 0.511 | 0.531 | 0.499 |

Notes:
µg/L = microgram(s) per liter.
Results compared to lowest of relevant thresholds—Level of Concern for the Grassland Bypass Project = 2 µg/L. (Beckon et al. 2008.) Exceedances would be shaded and in italics—there are no exceedances.
* All: Water years 1975–1991 represent the 16-year period modeled using DSM2. Drought: Represents a 5-consecutive year (water years 1987–1991) drought period consisting of dry and critical water-year types (as defined by the Sacramento Valley 40-30-30 water year hydrologic classification index).
These data are preliminary and are subject to change as BDCP analyses are finalized.

Selenium concentrations in fish tissue fillets (largemouth bass) for both the EBC_ELT/LLT and preliminary proposal (PP_ELT and PP_LLT) are listed in Table D-17 and Table D-18. These tables also provide estimates for drought years only, when there is potential for greater effects. Generally, concentrations for both the early and late long-term were slightly lower than the EBC. None of the fish tissue concentrations exceeded the Advisory Tissue Level (Office of Environmental Health Hazard Assessment 2008) of 2.5 mg/kg.

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## *No comments*

- n/a -

**Table D-17. Modeled Selenium Concentrations in Fish Fillets for Early Long-Term**

| Location | Period* | Period Average Concentration (mg/kg, ww) | | |
|---|---|---|---|---|
| | | Existing Conditions | EBC2_ELT | PP_ELT |
| **Delta Interior** | | | | |
| Mokelumne River (SF) at Staten Island | All | 0.35 | 0.35 | 0.32 |
| | Drought | 0.70 | 0.70 | 0.68 |
| San Joaquin River at Buckley Cove | All | 1.22 | 1.14 | 1.08 |
| | Drought | 1.95 | 1.74 | 1.59 |
| Old River at Rancho del Rio | All | 0.58 | 0.57 | 0.61 |
| | Drought | 0.79 | 0.78 | 0.75 |
| **Western Delta** | | | | |
| Sacramento River above Pt. Sacramento | All | 0.44 | 0.44 | 0.44 |
| | Drought | 0.74 | 0.73 | 0.73 |
| San Joaquin River at Antioch Ship Channel | All | 0.44 | 0.43 | 0.46 |
| | Drought | 0.66 | 0.66 | 0.65 |
| Sacramento River at Mallard Island | All | 0.33 | 0.33 | 0.33 |
| | Drought | 0.49 | 0.49 | 0.48 |
| | Drought | 1.34 | 1.35 | 1.27 |

Notes:
mg/kg = milligram per kilogram; ww = wet weight.
Results compared to Advisory Tissue Level = 2.5 mg/kg. (Office of Environmental Health Hazard Assessment 2008.) Exceedances are shaded and in italics—there are no exceedances.
* All: Water years 1975–1991 represent the 16-year period modeled using DSM2. Drought: Represents a 5-consecutive year (water years 1987–1991) drought period consisting of dry and critical water-year types (as defined by the Sacramento Valley 40-30-30 water year hydrologic classification index).
These data are preliminary and are subject to change as BDCP analyses are finalized.

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***No comments***

- n/a -

**Table D-18. Modeled Selenium Concentrations in Fish Fillets for Late Long-Term**

| Location | Period* | Period Average Concentration (mg/kg, ww) | | |
|---|---|---|---|---|
| | | Existing Conditions | EBC2_LLT | PP_LLT |
| **Delta Interior** | | | | |
| Mokelumne River (SF) at Staten Island | All | 0.35 | 0.35 | 0.33 |
| | Drought | 0.70 | 0.70 | 0.68 |
| San Joaquin River at Buckley Cove | All | 1.22 | 1.11 | 1.12 |
| | Drought | 1.95 | 1.67 | 1.72 |
| Old River at Rancho del Rio | All | 0.58 | 0.57 | 0.61 |
| | Drought | 0.79 | 0.80 | 0.77 |
| **Western Delta** | | | | |
| Sacramento River above Pt. Sacramento | All | 0.44 | 0.44 | 0.43 |
| | Drought | 0.74 | 0.73 | 0.73 |
| San Joaquin River at Antioch Ship Channel | All | 0.44 | 0.43 | 0.46 |
| | Drought | 0.66 | 0.66 | 0.66 |
| Sacramento River at Mallard Island | All | 0.33 | 0.33 | 0.33 |
| | Drought | 0.49 | 0.49 | 0.48 |
| | Drought | 1.34 | 1.40 | 1.31 |

Notes:
mg/kg = milligram per kilogram; ww = wet weight.
Results compared to Advisory Tissue Level = 2.5 mg/kg. (Office of Environmental Health Hazard Assessment 2008.) Exceedances would be shaded and in italics—there are no exceedances.
* All: Water years 1975–1991 represent the 16-year period modeled using DSM2. Drought: Represents a 5–consecutive year (water years 1987–1991) drought period consisting of dry and critical water-year types (as defined by the Sacramento Valley 40-30-30 water year hydrologic classification index).
These data are preliminary and are subject to change as BDCP analyses are finalized.

The elevated concentrations in fish under drought conditions of 4.68 mg/kg (EBC2_ELT) and 4.5 mg/kg (EBC2_LLT) were estimated to decrease under the preliminary proposal. Estimated concentrations of selenium decreased in whole-body fish for EBC2 and PP for both early long-term (ELT) and late long-term (LLT) are listed in Table D-19 and Table D-20. Modeled selenium concentrations under all scenarios were below the level of concern for whole-body fish (lower-end range) (Beckon et al. 2008) of 4 mg/kg, except at the San Joaquin River at Buckley Cove location.

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## *No comments*

- n/a -

1 **Table D-19. Modeled Selenium Concentrations in Whole-Body Fish for Early Long-Term**

| Location | Period* | Period Average Concentration (mg/kg, dw) | | |
|---|---|---|---|---|
| | | Existing Conditions | EBC2_ELT | PP_ELT |
| **Delta Interior** | | | | |
| Mokelumne River (SF) at Staten Island | All | 1.16 | 1.17 | 1.10 |
| | Drought | 2.06 | 2.06 | 2.00 |
| San Joaquin River at Buckley Cove | All | 3.38 | 3.18 | 3.01 |
| | Drought | *5.21* | *4.68* | *4.30* |
| Old River at Rancho del Rio | All | 1.76 | 1.74 | 1.84 |
| | Drought | 2.27 | 2.26 | 2.19 |
| **Western Delta** | | | | |
| Sacramento River above Pt. Sacramento | All | 1.39 | 1.39 | 1.40 |
| | Drought | 2.16 | 2.14 | 2.13 |
| San Joaquin River at Antioch Ship Channel | All | 1.39 | 1.39 | 1.45 |
| | Drought | 1.97 | 1.95 | 1.93 |
| Sacramento River at Mallard Island | All | 1.13 | 1.12 | 1.14 |
| | Drought | 1.53 | 1.52 | 1.50 |
| | Drought | 3.68 | 3.70 | 3.49 |

Notes:
dw = dry weight; mg/kg = milligram per kilogram.
Results compared to Level of Concern for whole-body fish (lower end range) = 4 mg/kg. (Beckon et al. 2008.) Exceedances are shaded and in italics.
* All: Water years 1975–1991 represent the 16-year period modeled using DSM2. Drought: Represents a 5–consecutive year (water years 1987–1991) drought period consisting of dry and critical water-year types (as defined by the Sacramento Valley 40-30-30 water year hydrologic classification index).
These data are preliminary and are subject to change as BDCP analyses are finalized.

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## *No comments*

- n/a -

**Table D-20. Modeled Selenium Concentrations in Whole-Body Fish for Late Long-Term**

| Location | Period* | Period Average Concentration (mg/kg, dw) | | |
|---|---|---|---|---|
| | | Existing Conditions | EBC2_LLT | PP_LLT |
| **Delta Interior** | | | | |
| Mokelumne River (SF) at Staten Island | All | 1.16 | 1.18 | 1.12 |
| | Drought | 2.06 | 2.07 | 2.01 |
| San Joaquin River at Buckley Cove | All | 3.38 | 3.10 | 3.13 |
| | Drought | *5.21* | *4.50* | *4.64* |
| Old River at Rancho del Rio | All | 1.75 | 1.73 | 1.84 |
| | Drought | 2.28 | 2.30 | 2.24 |
| **Western Delta** | | | | |
| Sacramento River above Pt. Sacramento | All | 1.39 | 1.39 | 1.39 |
| | Drought | 2.16 | 2.15 | 2.13 |
| San Joaquin River at Antioch Ship Channel | All | 1.39 | 1.38 | 1.44 |
| | Drought | 1.97 | 1.96 | 1.95 |
| Sacramento River at Mallard Island | All | 1.13 | 1.12 | 1.12 |
| | Drought | 1.53 | 1.53 | 1.50 |
| | Drought | 3.68 | 3.83 | 3.60 |

Notes:
dw = dry weight; mg/kg = milligram per kilogram.
Results compared to level of concern for whole-body fish (lower end range) = 4 mg/kg. (Beckon et al. 2008.) Exceedances are shaded and in italics.
* All: Water years 1975–1991 represent the 16-year period modeled using DSM2. Drought: Represents a 5-consecutive year (water years 1987–1991) drought period consisting of dry and critical water-year types (as defined by the Sacramento Valley 40-30-30 water year hydrologic classification index).
These data are preliminary and are subject to change as BDCP analyses are finalized.

**Uncertainty Analysis**

Modeling results are based on selenium water data for years 2010 and earlier. As previously discussed, selenium discharges from the Grassland watershed, a main contributor of selenium to the San Joaquin River and the Delta, must continue to decrease to meet relatively new criteria. The loading from the Grassland Project Area and resultant concentrations in the San Joaquin River are expected to continue to decline and will greatly diminish the source of selenium to the San Joaquin River and the Delta as a whole. The water and fish tissue modeling results does not account for this future decrease in selenium in the system and likely overestimates concentrations with the preliminary proposal water operations.

### D.5.2.2.3 Changes in Proportion of San Joaquin Water in the Delta

Because the San Joaquin watershed historically has been a major source of selenium to the Delta, there is a concern that water operations, and specifically reduced flows in the Sacramento River, under the preliminary proposal could result in an increased proportion of San Joaquin water in the Delta, and with it increased selenium concentrations. DSM2 model results were used to track source water in the Delta. Results showing the difference in annual average contribution from the San

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## *No comments*

- n/a -

Joaquin River in the south Delta and Suisun Bay are presented in Table D-21. South Delta was chosen because of its proximity to the San Joaquin River. Suisun Bay was selected because elevated levels of selenium have been detected, mainly in biota, in the area. Also, Suisun Bay is near oil refineries where elevated selenium concentrations have been an issue.

**Table D-21. Difference in Annual Average Proportion of San Joaquin River Contribution to Water Flow at South Delta and Suisun Bay**

| | South Delta—Change in San Joaquin River Contribution | | Suisun Bay—Change in San Joaquin River Contribution | |
|---|---|---|---|---|
| | Percent Difference EBC2_ELT to PP_ELT | Percent Difference EBC2_LLT to PP_LLT | Percent Difference EBC2_ELT to PP_ELT | Percent Difference EBC2_LLT to PP_LLT |
| 1976 | -1 | -2 | 0 | 0 |
| 1977 | -4 | -1 | 0 | 0 |
| 1978 | 14 | 15 | 2 | 2 |
| 1979 | 5 | 6 | 1 | 1 |
| 1980 | 6 | 7 | 1 | 1 |
| 1981 | -3 | -4 | 0 | 0 |
| 1982 | 17 | 21 | 4 | 3 |
| 1983 | 22 | 19 | 9 | 7 |
| 1984 | 12 | 14 | 5 | 5 |
| 1985 | -2 | -3 | 0 | 0 |
| 1986 | 6 | 6 | 1 | 1 |
| 1987 | -7 | -5 | 0 | 0 |
| 1988 | 0 | 3 | 0 | 0 |
| 1989 | -1 | 8 | 0 | 0 |
| 1990 | -1 | -1 | 0 | 0 |
| 1991 | -2 | -7 | 0 | 0 |
| Average | 4 | 5 | 1 | 1 |

Results presented in Table D-21 show variation in the south Delta. The preliminary proposal actions would result in a less than 10% annual average increase in San Joaquin River water in the south Delta relative to other source waters (including the Sacramento River). For water years 1978, 1982, 1983, and 1984, the proportion of San Joaquin water is higher (12 to 22%). Preliminary proposal actions will have little to no effect on the proportion of San Joaquin water that flows to Suisun Marsh. Again, 1983 has the highest proportion of San Joaquin water present (9% for ELT and 7% for LLT).

### D.5.2.3 Restoration

In addition to preliminary proposal water operations effects described above, selenium concentrations in water and covered fish tissues may be affected by mobilization of selenium in restoration areas. Because the bioavailability of selenium increases in an aquatic system, inundation of ROAs could mobilize selenium sequestered in sediments and increase exposure of covered fish species. The rate at which selenium will become mobilized as part of restoration will depend on the amount of selenium stored in the sediments, the length of inundation, and whether sufficient time



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## *No comments*

- n/a -

allows the selenium to cycle through the aquatic system and into the food chain. It is likely that the highest concentrations of selenium will be mobilized during the initial flooding but will taper off with time; the length of time for the majority of selenium to flush out is not currently known and would need to be evaluated on a site-specific basis. Given that the San Joaquin River historically has delivered selenium to the Delta, the South Delta ROA has the most potential for mobilization of selenium.

In the long term, selenium inputs to the Delta should decrease as the proportion of agricultural lands decreases as a result of land use changes, including restoration to marsh habitat by the BDCP; selenium no longer would be concentrated by irrigation and leaching of these formerly farmed areas. This is especially true of the south Delta, where selenium in near-surface soils could be mobilized, but additional concentration from irrigation will cease. In contrast to the benefit of stopping application of pesticides to restored farmland, the benefit associated with selenium likely will be low, as selenium actually is leached out of the soils by agricultural use, not applied.

#### D.5.2.3.1 Selenium Summary

Quantitative modeling of selenium concentrations suggests that the preliminary proposal water operations would have from no effect to a positive effect on selenium in water and fish tissues. The only exceedances for fish tissues were for fish fillets and whole-body fish at Buckley Cove on the San Joaquin River during drought conditions. At Buckley Cove, benchmarks were exceeded for existing conditions (EBC2) and existing conditions early long-term (EBC2_ELT); the early long-term concentrations were lower under the preliminary proposal (PP_ELT). It is not surprising that the highest concentrations of selenium were estimated for the San Joaquin River, as this is the recognized primary source of selenium to the Delta. Future required reductions in selenium sources in the San Joaquin watershed should result in lower concentrations than those estimated by the model.

Source-water fingerprinting analysis indicates that preliminary proposed water operations will not result in a significant increased proportion of San Joaquin water at Suisun Bay. Proportions of San Joaquin water in the south Delta could increase by as much as 20%. Given the expected decrease in selenium contributions from the San Joaquin River and modeling results indicating that selenium concentrations will not exceed criteria in the south Delta, no effects on selenium concentrations as a result of preliminary proposal water operations are identified.

Selenium currently sequestered in soils could be mobilized and become more bioavailable as a result of inundation of restoration areas. The magnitude of this mobilization of selenium and resultant increases in concentrations in both water and covered species would need to be determined on a site-specific basis. The potential is highest for increased mobilization of selenium in and near the San Joaquin River and the South Delta ROAs, where selenium concentrations in soils are expected to be highest.

## D.5.3 Copper

### D.5.3.1 Copper—Location, Environmental Fate, and Transport

Copper (Cu) is a naturally occurring element that is present in water, air, and many soils in the environment. It is an essential trace element required by many plants and animals at low concentrations but can be toxic at elevated concentrations. In a non-aqueous environment, copper



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***No comments***

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tends to adhere to soils and is relatively immobile. In an aqueous system, copper is considered one of the more mobile heavy metals. It partitions between sediment and particulates, and as particulates, it is taken up by low trophic levels or complexes with organics or inorganics in the water column. Typically it will occur in one of two oxidation states, cuprous ion ($Cu^{1+}$) and cupric ion ($Cu^{2+}$) (U.S. Environmental Protection Agency 2009). Toxicity is much higher for the $Cu^{2+}$ ion, than for the $Cu^{1+}$ ion and the copper that is organically complexed (Buck et al. 2007; Manahan and Smith 1973; Sunda and Guillard 1976).

Although copper is not listed in the 303(d) list in the Delta, it is of concern mainly because of its widespread use in pesticides. In the Delta, anthropogenic sources of copper include pesticides/herbicides, mine drainage, brake pads, and anti-foulants (such as paint used on boat bottoms) (U.S. Environmental Protection Agency 2009). Because agriculture is the dominant land use in the Delta, use of pesticides/herbicides is a dominant source of copper to the environment. Mine drainage also has been a historical source of copper to the Delta. The Iron Mountain Mines Superfund Site, a former mine that released acid mine drainage to the Sacramento River upstream of Keswick Dam, has been a significant source of copper and other metal contamination. However, the Superfund Site is undergoing remediation that has decreased discharge of copper into the rivers, and a TMDL has been implemented (Central Valley Regional Water Quality Control Board 2002). Following remediation, copper inputs from this mine should continue to decrease.

The current AWQC-Fresh Water-Chronic for copper in fresh water is derived on a site-specific basis requiring the input of 10 separate site-specific parameters to calculate the criteria—temperature, pH, DOC, calcium, magnesium, sodium, potassium, sulfate, chloride, and alkalinity. Because these parameters vary depending on location, it is not possible to calculate a general AWQC-Fresh Water-Chronic for copper.

Overall, levels of copper in the Delta ecosystem do not appear to be significantly elevated. Copper concentrations in the Sacramento River have been reported to be consistently low, with some seasonal fluctuation (Connon 2010; Domagalski 2008). Based on collection of 549 water samples collected during critically dry, normal, and wet years from 15 Delta stations, metals concentrations did not exceed AWQC and did not show toxicity (Central Valley Regional Water Quality Control Board 1998).

Bruns (1998) conducted water sampling between 1993 and 1995, compared both dissolved and total copper results against EPA AWQC and other criteria, and reported concentrations below criteria from almost all locations, including the Sacramento River. Because the criteria are dependent on sample-specific water quality measurements (including hardness), the criteria varied between sampling episodes. Significantly higher copper levels (at least an order of magnitude higher than all other results) that exceeded criteria were reported for Prospect Slough at the head of the Yolo Bypass.

In general, the copper data sets discussed above indicate low levels of copper (less than 2 µg/L) throughout the Delta waterways and elevated concentrations in agricultural drainage sloughs, and in tributaries at the head of the Yolo Bypass.



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### D.5.3.2 Copper—Effects of Preliminary Proposal Conservation Measures

#### D.5.3.2.1 Water Operations

Preliminary proposal water operations will result in decreased flow in the Sacramento River under certain conditions. However, because copper concentrations are consistently low throughout the Sacramento River (less than 2 µg/L) and copper concentrations in the Sacramento River watershed have been tied to flow rates, appreciable impact on copper concentrations is not expected.

#### D.5.3.2.2 Restoration

Restoration of agricultural lands under the preliminary proposal will have two outcomes relative to copper: copper contained in soils may become more bioavailable, and copper in pesticides that would have been applied to the agricultural land will be subtracted from the total Delta copper loads.

In general, the copper data sets discussed above indicate low levels of copper (less than 2 µg/L) throughout the Delta waterways, and elevated concentrations in agricultural drainage sloughs. Although data were not identified, it is assumed the agricultural soils will contain some level of copper given its affinity for soils in a terrestrial environment. A study of copper mobilization and bioavailability following multiple floodings of copper-enriched agricultural soils in the Everglades (Hoang et al. 2008) presents some relevant findings: (1) the amount of copper mobilized into the aquatic system depended on the concentrations in the soils, DOC, alkalinity, and soil characteristics; (2) copper concentrations in soils did not change much after multiple (four) floodings; (3) total dissolved copper in the water column did not decrease after several flooding events; and (4) the proportion of the more toxic cupric ion ($Cu^{2+}$) increased with the number of flooding episodes and decreased DOC.

These findings suggest that formerly agricultural ROAs, which are likely to have elevated levels of copper in soils, will result in some level of increased copper in the aquatic system over an undetermined time period. Currently, information on the concentrations of copper in soils of specific ROAs is insufficient to estimate the increase in concentrations.

Restoration of agricultural land to marshes and floodplains will result in decreased application of copper-containing pesticides and decreased copper loading to the Delta. This net benefit at least partially will counter the copper introduced to the aquatic system through mobilization during inundation.

## D.5.4 Ammonia/um

### D.5.4.1 Ammonia/um—Location, Environmental Fate, and Transport

Ammonia is present in water in two forms: as un-ionized ammonia ($NH^{3+}$), also sometimes referred to as free ammonia, and as a positively charged ammonium ion ($NH^{4+}$). These two forms are collectively referred to as total ammonia or ammonia plus ammonium. Generally, environmental un-ionized ammonia is more toxic to fish, and ammonium is taken up by plants and algae as a nutrient and can drive algae blooms and growth of invasive species (Jabush 2011).

The primary source of total ammonia in the Delta is effluent discharged from WWTPs, and the primary contributing treatment facility is the Sacramento Regional WWTP (Jassby 2008). The



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Sacramento plant is the source of the largest wastewater effluent discharge to the Delta (Jassby 2008), contributing an average of 141 million gallons per day (mgd) and accounting for 1 to 2% of the river water volume (Foe et al. 2010). The facility is also the largest source of total ammonia discharge to the Delta, making up 90% of the Sacramento River ammonia load (Jassby 2008). The Stockton Regional Wastewater Control Facility historically had been an important source of the ammonia load to the Delta via the San Joaquin River. This is no longer the case, as the Stockton facility has upgraded its treatment systems in recent years to include technology to remove ammonia and ammonium from effluent before discharge to the river (City of Stockton 2011).

For ammonia, there is a current EPA AWQC dated 1999, and an updated draft AWQC dated 2009 that has not yet been finalized (Table D-22). Both the current (1999) and draft (2009) AWQC for total ammonia as nitrogen are dependent on site-specific temperature and pH. The draft AWQC is also dependent on the presence or absence of unionid mussels. AWQC for ammonia (total as N) for both the current criteria and the draft criteria are listed in Table D-22. For ease of comparison, only AWQC at a temperature of 25°C and pH of 8 are listed.

**Table D-22. Ambient Water Quality Criteria for Ammonia**

| | Draft 2009 Ammonia Criteria (at pH 8 and 25°C) | Current 1999 Ammonia Criteria (at pH 8 and 25°C) |
|---|---|---|
| Acute | 2.9 mg N/L mussels present | 5.6 mg N/L salmon present |
| | 5.0 mg N/L mussels absent | |
| Chronic | 0.26 mg N/L mussels present | 1.2 mg N/L fish early life stages present |
| | 1.8 mg N/L mussels absent | |
| Source: <http://water.epa.gov/scitech/swguidance/standards/criteria/aqlife/pollutants/ammonia/factsheet2.cfm>. | | |

A recent study indicated that biota can be affected at concentrations as low as 0.38 mg/L of total ammonia nitrogen, based on a study of Delta copepods by Teh and coauthors (2011).

The current NPDES permit (2010) for the Sacramento WWTP contains both new and interim standards for ammonia. The current NPDES permit also prohibits discharge to the Sacramento River when there is less than a 14:1 (river:effluent) flow ratio over a rolling 1-hour period available in the Sacramento River. In addition, to comply with new standards (Table D-23), the Sacramento plant will need to install new systems to reduce ammonia concentrations in effluent. Compliance with new effluent limits will be required as of December 1, 2020, or once the new systems are in place, whichever occurs first (Central Valley Regional Water Quality Control Board 2010). However, this permit is being appealed and may not be upheld.



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**Table D-23. Sacramento and Stockton Wastewater Treatment Facility Effluent—National Pollution Discharge Elimination System Permit Limits**

| | Units | Sacramento Effective 2010 (Interim) Average Daily | Sacramento Effective 2020 (New) Average Daily |
|---|---|---|---|
| Ammonia, total as N | mg/L | 33 | 1.8 |
| | lb | 49,400 | 2,720 |
| Design flow | mgd | 181 | 181 |
| Source: Central Valley Regional Water Quality Control Board 2010. | | | |

The Sacramento Regional County Sanitation District (2011) reported the following ammonia concentrations in effluent from the Sacramento WWTP for the year 2010: average 24 mg/L (parts per million [ppm]); minimum 19 mg/L; and maximum 39 mg/L. Along with influent and effluent testing, the new 2010 NPDES permit requires that the Sacramento River (effluent-receiving water) be tested for ammonia, along with other parameters.

Ammonia concentrations in the Sacramento River were evaluated during a monitoring program conducted in 2009 and 2010. Water samples were collected on a monthly basis from 21 locations throughout the Delta, with a focus on tracking concentrations of ammonia downstream of the Sacramento WWTP (Foe et al. 2010). None of the ammonia data collected for 344 samples over 1 year exceeded the EPA chronic criterion for early life stages of fish present in the Delta (Foe et al. 2010). Results of this study indicated elevated ammonia levels immediately downstream of the Sacramento WWTP, with almost all the ammonia attenuated 20 miles downstream of the discharge, as follows:

- Ammonia concentrations were higher downstream (highest average 0.46 mg/L) of the Sacramento WWTP than upstream (average 0.04 mg/L).
- The highest ammonia concentrations were detected at Hood, 7 miles downstream of the WWTP.
- Downstream of Hood, total ammonia concentrations dropped continuously to an average of 0.08 mg/L at Threemile Slough, 20 miles downstream of the WWTP.

### D.5.4.2 Ammonia/um—Effects of Preliminary Proposal Conservation Measures

#### D.5.4.2.1 Water Operations

Given the possible link established between ammonia from WWTPs and the POD (Dugdale et al. 2007; Wilkerson et al. 2006; Glibert 2010; Glibert et al. 2011), decreased dilution capacity of the Sacramento River and potential resultant increases in ammonia concentrations are of concern. Recent data (Foe et al. 2010) indicate that concentrations of ammonia downstream of the WWTP outfall do not currently exceed EPA AWQC. These conditions are maintained with a current allowed ammonia concentration in WWTP effluent of 33 mg/L (and measured maximum concentration of 39 mg/L). By 2020, effluent must be below 1.8 mg/L ammonia, an 18-fold decrease in ammonia concentrations. It would take a similar decrease in Sacramento River flows to achieve the current conditions, and few to no effects are expected from preliminary proposal actions on ammonia/um. This conclusion is supported by the following quantitative analysis.



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To evaluate resultant ammonia concentrations in the Sacramento River, the average reported concentration of ammonia in Sacramento WWTP effluent (24 mg/L) was used to calculate the Sacramento River flow required to meet AWQC. As shown in Table D-24, the minimum flow in the Sacramento River needed to dilute effluent and meet the current AWQC of 1.2 mg/L in the Sacramento River would be 5,794 cubic feet per second (cfs).

**Table D-24. Sacramento River Flow Required to Dilute Sacramento Wastewater Treatment Plant Effluent**

| | |
|---|---|
| Average Effluent Ammonia Concentration | 24 mg/L |
| Design flow | 181 mgd (7,930.087 l/sec) |
| Ammonia load | 190,322.1 mg/sec |
| River—Threshold not to exceed | 1.2 mg/L |
| River—Upstream concentration | 0.04 mg/L |
| River—Threshold not to exceed | 1.16 mg/L |
| Threshold flow to exceed (river) | 164,070.8 l/sec (5,794 cfs) |

The DSM2 model output was analyzed to evaluate the percentage of time the minimum flow rate of 5,794 cfs would not be met. Results are presented in Table D-25 and Table D-26. Table D-25 presents the percentage of months the minimum flow would not be met for each scenario. Table D-26 shows the difference between EBC2_ELT and LLT and the preliminary proposal (PP_ELT and LLT) in the percent of time that Sacramento River flows at Freeport would fall below the required flow to dilute effluent. The effects of the preliminary proposal over the 82-year model run would be a 1.2% increase in the times that flows would be insufficient to meet AWQC for ammonia in August, and a 2.4% increase in October. In all other months, either no effects or a positive effect is indicated. The scenario is conservative, as concentrations in ammonia in Sacramento WWTP effluent are under order to decrease significantly.

In conclusion, changes in dilution capacity of the Sacramento River under the preliminary proposal would result from changes in upstream reservoir operations and are not expected to be significant. Diversion of water to the Yolo Bypass is not expected to affect dilution capacity, as this will occur only during high river flows. The north Delta intake is downstream of Freeport and will not affect dilution of Sacramento WWTP discharges.

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**Table D-25. Percentage of Months in CALSIM (82 Years) That Flows Are below Threshold (5,794 cfs) for Adequate Dilution of Sacramento WWTP Effluent to <1.2 mg/L Ammonia**

| | Percentage of Months with Inadequate Flows | | | | |
|---|---|---|---|---|---|
| Month | EBC2 | EBC2_ELT | EBC2_LLT | PP_ELT | PP_LLT |
| January | 0.0% | 0.0% | 0.0% | 0.0% | 0.0% |
| February | 0.0% | 0.0% | 0.0% | 0.0% | 0.0% |
| March | 0.0% | 0.0% | 0.0% | 0.0% | 0.0% |
| April | 0.0% | 0.0% | 0.0% | 0.0% | 0.0% |
| May | 1.2% | 1.2% | 2.4% | 1.2% | 2.4% |
| June | 0.0% | 0.0% | 0.0% | 0.0% | 0.0% |
| July | 0.0% | 0.0% | 0.0% | 0.0% | 0.0% |
| August | 0.0% | 0.0% | 0.0% | 1.2% | 0.0% |
| September | 0.0% | 1.2% | 2.4% | 0.0% | 0.0% |
| October | 0.0% | 2.4% | 0.0% | 0.0% | 2.4% |
| November | 0.0% | 0.0% | 2.4% | 0.0% | 1.2% |
| December | 0.0% | 0.0% | 0.0% | 0.0% | 0.0% |

**Table D-26. Percent Increase in the Number of Months That Flows Are below Threshold (5,794 cfs) for Adequate Dilution of Sacramento WWTP Effluent to <1.2 mg/L Ammonia**

| Month | EBC2_ELT-PP_ELT | EBC2_LLT-PP_LLT |
|---|---|---|
| January | 0.0% | 0.0% |
| February | 0.0% | 0.0% |
| March | 0.0% | 0.0% |
| April | 0.0% | 0.0% |
| May | 0.0% | 0.0% |
| June | 0.0% | 0.0% |
| July | 0.0% | 0.0% |
| August | -1.2% | 0.0% |
| September | 1.2% | 2.4% |
| October | 2.4% | -2.4% |
| November | 0.0% | 1.2% |
| December | 0.0% | 0.0% |

#### D.5.4.2.2 Restoration

Restoration conservation measures are not expected to significantly affect distribution or levels of ammonia/um in the Delta. Nitrogen is associated with fertilizers, which are used heavily throughout the Delta. However, WWTPs have been identified as the primary sources of ammonia, contributing 90% of the ammonia load to the Sacramento River. Thus, restoration of agricultural lands to marsh and floodplain is not expected to significantly affect ammonia concentrations.

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## D.5.5 Pyrethroids

### D.5.5.1 Pyrethroids—Location, Environmental Fate, and Transport

Pyrethroids are a group of synthetic chemicals currently used as insecticides in urban and agricultural areas. More than 1,000 synthetic pyrethroids have been developed (ASTDR 2003), but only 25 are registered for use in California (Spurlock and Lee 2008). Pyrethroids are powerful neurotoxins, have immunosuppressive effects, and can inhibit essential enzymes such as ATPases (Werner and Orem 2008). Pyrethroids can cause acute toxicity at concentrations as low as 1 µg/L in fish (Werner and Orem 2008), and at lower levels between 2 and 5 ng/L (0.002 and 0.005 µg/L) in invertebrates. When various types of pyrethroid compounds are present together in an aqueous environment, the toxicity can be additive with increased toxic effects (Weston and Lydy 2010).

Overall pyrethroid use in the Delta has nearly quadrupled from 1990 to 2006 from approximately 27,000 kilograms per year (kg/yr) to more than 101,000 kg/yr in 2006 (U.S. Department of the Interior 2008) with five pyrethroids (lambda-cyhalothrin, permethrin, esfenvalerate, cypermethrin, and cyfluthrin) among the top agricultural insecticides in California (by acres treated) (Werner and Orem 2008). Pyrethroids are found in agricultural runoff, urban stormwater runoff, and in public WWTP effluent.

Significant sources of pyrethroids coming into the Delta from agricultural land include summer irrigation return flows from treated areas, winter stormwater runoff from orchards as a result of the common practice of applying pyrethroids during the winter season, and draining of excess surface water from rice fields during cultivation (Oros and Werner 2005). In addition to agricultural sources, recent studies have shown that WWTPs and urban runoff are important sources of pyrethroids to the Delta system (Weston and Lydy 2010). Pyrethroids have been detected at concentrations lethal to amphipods in urban runoff and effluent from the Stockton, Vacaville, and Sacramento WWTPs (Weston and Lydy 2010). However, receiving waters (San Joaquin River, American River, and Sacramento River) had fewer detections of pyrethroids at sublethal concentrations. Concentrations were higher in Vacaville creeks receiving effluent.

Pyrethroids have low water solubility; they do not readily volatilize and have a tendency to bond to particulates, settle out into the sediment, and not be transported far from the source. Once pyrethroids enter the Delta, they are easily adsorbed to suspended particles, organic material, soil, and sediments (Oros and Werner 2005). Because of the low-solubility nature of pyrethroids, it is estimated that 94% of pyrethroids used in the Central Valley remain at the application site and almost 6% degrade, with half life (the average time it takes for the concentration of the chemical to be reduced by one half) ranging from days to months, leaving only 0.11% ultimately available for transport through the Delta (Werner and Orem 2008). Seventy sediment samples were collected from agricultural drainage–dominated irrigation canals that run through 10 Central Valley counties. Analysis showed pyrethroids in 75% of the samples (Weston et al. 2004). However, pyrethroids were not often detected in agricultural drainage waters, demonstrating their strong affinity to sediments (Weston 2010).

Because pyrethroids have a very strong affinity for particulates, benthic organisms may be exposed to pyrethroids in sediment, and pelagic species could be exposed to pyrethroids adsorbed to particulates in the water column. Because pyrethroids are lipophilic, they have a tendency to bioaccumulate through the food chain (Werner and Orem 2008).



***No comments***

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Breakdown of pyrethroids can occur through both chemical and biological processes and can take from days to months depending on a number of factors (Werner and Orem 2008). Half lives of pyrethroids are influenced by temperature and pH. At an alkaline pH, some pyrethroids can degrade through hydrolysis; however, most are stable at the relatively neutral pH of Delta waters (Werner and Oram 2008).

Many pyrethroids also are susceptible to degradation by sunlight, called photodegradation. The half life of different pyrethroids in water varies greatly with differences in their susceptibility to sunlight, from 0.67 day for cyfluthrin to 600 days for fenpropathrin (Werner and Oram 2008). High turbidity and the presence of plants can reduce ultraviolet-light penetration and increase pyrethroid half life, allowing increased residence times and the potential for greater adsorption to sediment.

### D.5.5.2 Pyrethroids—Effects of Preliminary Proposal Conservation Measures

#### D.5.5.2.1 Water Operations

As discussed above for ammonia, preliminary proposal water operations will result in reductions in Sacramento River flow at Freeport under certain conditions, mainly due to upstream reservoir operations. This reduction in flow could limit the dilution of Sacramento WWTP effluent and urban runoff, resulting in increased pyrethroid concentrations affecting covered fish species. In their study of pyrethroids in urban runoff, WWTPs, and receiving waters, Weston and Lydy (2010) reported few to no detections or toxicity to amphipods in Sacramento River water downstream of the Sacramento WWTP.

Weston and Lydy (2010) estimated loading from the Sacramento WWTP at 9g/day in the dry season and 13 g/day in the wet season. These estimates were based on median detected levels of total pyrethroids in effluent from three dry-weather (18.2 ng/L) and three wet-weather (14.2 ng/L) sampling events. Using a 13 g/day pyrethroid load and the lowest flow rate in the Sacramento River at Freeport in an 82-year period, estimated by the DSM2 at 5,110 cfs, the resultant concentration of pyrethroids in the Sacramento River is 7.19885 E-07 ng/L. This is consistent with Weston and Lydy's (2010) results that showed little to no detection of pyrethroids in the Sacramento River (Table D-27).

**Table D-27. Estimation of Resultant Pyrethroid Concentrations in Water under Preliminary Proposal Low-Flow Conditions in the Sacramento River**

| | | | |
|---|---|---|---|
| Pyrethroid Loading from Sacramento WWTP (Weston and Lydy 2010) | 9 g/day | = 0.000104167 g/s | =0.104167 ng/s |
| Minimum Flow over 82 years with Preliminary Proposal | 5,110 cfs | = 144,698.9497 L/sec | |
| Resultant Concentration | 7.19885E-07 ng/L | Pyrethroids in the Sacramento River | |

Based on this analysis, the preliminary proposal water operations will have no effects on pyrethroids.



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#### D.5.5.2.2 Restoration

As discussed above, pyrethroids have been applied widely to agricultural land across the Delta; they tend to stay sequestered in soils and therefore will be present in ROA soils. Pyrethroids have a strong affinity for particulates, and would enter the water column as suspended particulates that likely would settle out over time. The lack of pyrethroids in surface water samples where they are present in sediments (Weston et al. 2004; Weston and State Water Resources Control Board 2010) demonstrates the strong propensity for pyrethroids to remain in sediment. During inundation of restoration areas, pyrethroids could be mobilized in the food chain via uptake by benthic organisms or uptake of particulates by pelagic organisms.

Current information does not allow estimation of resultant pyrethroid mobilization due to preliminary proposal restoration. Concentrations of pyrethroids in ROA sediments and additional research on mobilization and uptake into the food chain would be required. Given their affinity for soils, pyrethroids are not expected to spread far from the source area, and any suspension into the water column should be localized.

## D.5.6 Organochlorine Pesticides

### D.5.6.1 Organochlorine Pesticides—Environmental Fate and Transport

Organochlorine pesticides, specifically DDT, chlordane, and dieldrin, are legacy pesticides that are no longer in use but persist in the environment (Werner et al. 2008). These pesticides came into use from the late 1930s to the late 1940s and were phased out for general use in the 1970s; however, both chlordane and dieldrin remained in use until the late 1980s for termite control (Connor et al. 2007). These pesticides are widespread throughout the Sacramento and San Joaquin River watersheds and the Delta from widespread agricultural use (Conner et al. 2007).

Organochlorine pesticides have a very low solubility in water and are very persistent in the environment. DDT will degrade to dichlorodiphenyldichloroethane (DDD) and dichlorodiphenyldichloroethene (DDE), but these toxic by-products have very long half lives. The Central Valley Water Board Agricultural Waiver Program recently reported detections of DDT and other organochlorine pesticides in Delta agricultural ditches and drainage channels (Werner et al. 2008). Because they do not dissolve in water, organochlorine pesticides enter the food chain in particulate form, mainly through uptake by benthic fauna. They are strongly lipophilic and biomagnify through the food chain, resulting in high concentrations in high trophic levels.

The current AWQC-Fresh Water-Chronic for the organochlorine pesticides of concern in the Delta—DDT, chlordane, and dieldrin—are 0.001, 0.0043, and 0.056 µg/L, respectively. It should be noted, however, that the EPA anticipates future revisions to the criteria.

The highest concentrations in sediments and the greatest loading of organochlorine pesticides are thought to come from the western tributaries of the San Joaquin River, and high concentrations have been reported in San Joaquin River sediments (Gilliom and Clifton 1990 cited in Domagalski 1998). However, total concentrations in the water column were low, consistent with the strong affinity of organochlorine pesticides for sediments. Domagalski (1998) reported low concentrations in the water column in the San Joaquin River basin, and noted that the organochlorine pesticides were highest in tributary sediments and appeared to be mobilized by storms and rainfall. A study involving collection and analysis of 70 sediment samples over 10 counties in the Central Valley showed that organochlorine pesticides continue to be present in sediments, and at high



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concentrations, especially in agricultural drainage canals (Weston et al. 2004). This study found DDT in almost all samples collected, with a median concentration of 6.9 ng/g, and a maximum concentration of 408 ng/g in a drainage canal. DDE and other organochlorine pesticides also were detected at high levels in other drainage canal sediments.

### D.5.6.2 Organochlorine Pesticides—Effects of Preliminary Proposal Conservation Measures

#### D.5.6.2.1 Water Operations

Preliminary proposal water operations are not likely to result in mobilization of organochlorine pesticides. In the San Joaquin watershed, where concentrations are highest, these chemicals are found primarily in sediments in tributaries draining agricultural areas, and are present at low concentrations in the water column. Preliminary proposal water operations would not result in increased flows in the tributaries that would mobilize organochlorine pesticides in sediments. No changes in the load or concentrations of organochlorine pesticides transported into the Delta by the San Joaquin River are anticipated.

Upstream reservoir operations under the preliminary proposal will result in decreased flows in the Sacramento River, as discussed in previous sections. Because organochlorine pesticides adhere to soils, mobilization would have to be facilitated by erosion of contaminated soils. As significant increases in flow velocity are not expected under the preliminary proposal, organochlorine pesticides are not expected to be mobilized. Thus, no effects on organochlorine pesticide distribution are expected under the preliminary proposal water operations.

#### D.5.6.2.2 Restoration

Organochlorine pesticides likely will be sequestered in the formerly agricultural soils in ROAs. The highest concentrations will be in the ditches, creeks, and drains that received agricultural discharges. Because these chemicals tend to bind to particulates, concentrations are typically highest in sediment. Flooding of formerly agricultural land is expected to result in some level of accessibility to biota through uptake by benthic organisms. Significant increases in organochlorine pesticides are not expected in the water column because these chemicals strongly partition to sediments. Exposures to the foodweb will be through intake by benthic fauna and to a lesser extent, through particulates in the water column to pelagic organisms.

Also, concentrations in the water column should be relatively short-lived because these pesticides settle out of the water column in low-velocity flow. If eroded and transported from an ROA, it is likely that the pesticides would not be transported very far from the source area and would settle out and be deposited close to the ROA.

## D.5.7 Organophosphate Pesticides

### D.5.7.1 Organophosphate Pesticides—Environmental Fate and Transport

Organophosphate pesticides (organophosphates) are human-made chemicals that are used for pest control in both urban and agricultural environments. Sources of diazinon and chlorpyrifos in the Delta are predominantly agricultural as the sale of these compounds for most nonagricultural uses has been banned in recent years. In the Delta, diazinon is applied to crops during the dormant



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season (December–February) and irrigation or growing season (March–November) fairly equally (52% and 48%, respectively), while the majority of chlorpyrifos (97%) is applied to Delta crops during irrigation season (McClure et al. 2006).

Diazinon and chlorpyrifos have slightly different chemical properties that affect the way they behave in aquatic environments. Diazinon is fairly soluble and mobile and will bind only weakly to soil and sediment. Chlorpyrifos is less soluble than diazinon and less mobile because of its tendency to bind much more strongly to soil and sediment. Consequently, diazinon enters the Delta dissolved in runoff, while chlorpyrifos enters the Delta adsorbed to soil particles (McClure et al. 2006). Unlike organochlorine pesticides, organophosphates do not tend to bioaccumulate, as they are readily metabolized by most organisms. For example, diazinon in fish will be approximately 96% removed in just 7 days (McClure et al. 2006).

Surface water data indicate that concentrations are high for both diazinon and chlorpyrifos in back sloughs and small upland drainages, and concentrations are lower in both the main channels and main inputs to the Delta. High concentrations of chlorpyrifos also are found in Delta island drains, but concentrations of diazinon remain low in the same drains (McClure et al. 2006). In the past, elevated concentrations of diazinon and chlorpyrifos have been detected in the Sacramento and San Joaquin Rivers and in the Delta during particularly wet springs and after winter storm events (McClure et al. 2006), suggesting that increased flow with accompanying increased suspended loads will result in increased mobilization of both diazinon and chlorpyrifos.

In the 2006 Staff Report for the amendments to the Basin Plan for diazinon and chlorpyrifos, updated water quality objectives developed by California Department of Fish and Game for diazinon and chlorpyrifos were compared to a broad sample set (McClure et al. 2006). Authors summarize surface water data for diazinon from 1991 to 2005, and chlorpyrifos from 1988 to 2005, from a number of previous sampling programs and studies and compared results to the updated water quality objectives of 160 and 25 ng/L for diazinon and chlorpyrifos, respectively. For context, the current AWQC-Fresh Water-Chronic for diazinon is 170 ng/L (0.17 µg/L). There is no AWQC-Fresh Water-Chronic for chlorpyrifos.

Locations where diazinon exceeded 160 ng/L in more than 10% of samples included Mosher Slough, San Joaquin River near Stockton, Stockton Diverting Channel, and French Camp Slough. Likewise chlorpyrifos results showed more than 10% of samples collected at these locations exceeded 25 ng/L, including Ulatis Creek, Mosher Slough, Middle Roberts Island Drain, French Camp Slough, Paradise Cut, and Stockton Diverting Channel.

### D.5.7.2 Organophosphate Pesticides—Preliminary Proposal Conservation Measures

#### D.5.7.2.1 Water Operations

Diazinon and chlorpyrifos concentrations are highest in the back sloughs and agricultural drains that receive agricultural drainage. Preliminary proposal water operations are not likely to have much effect on transport of these chemicals from the back areas; transport of the pesticides from these areas would be determined mostly by rains that would flush out the areas. When flushed during wet seasons, the Sacramento River would maintain the capacity to dilute the influx. As discussed in Section D.5.4 (*Ammonia/um*), reduced flows would occur during dry periods in the



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Sacramento River, when the back tributaries would not be flushing out. In general, preliminary proposal water operations are not expected to affect organophosphate concentrations in the Delta.

#### D.5.7.2.2 Restoration

Organophosphate pesticides are likely present in ROA soils that would be inundated under preliminary proposal conservation measures. Because the solubility, tendency to adhere to soils and particulates, and degradation rates for these compounds vary, it is difficult to estimate the extent to which inundation would cause the toxins to be mobilized and more bioavailable in the aquatic system. Also, because organophosphate pesticides are metabolized by fish and do not bioaccumulate, effects on covered species would be limited, depending on the life stage.

### D.5.7.3 Herbicides Associated with Conservation Measure 13 Nonnative Aquatic Vegetation Control

CM13 Nonnative Aquatic Vegetation Control would involve applying existing methods used by the California Department of Boating and Waterways' (DBW's) *Egeria densa* and Water Hyacinth Control Programs. Following is a brief summary of the types of herbicides used and the known toxic effects. (Table D-28.)

DBW uses five common herbicides—Weedar 64® (2,4-D), Rodeo® (glyphosate), R-11® (NP & NPE), Sonar® (fluridone), and Reward® (diquat). Riley and Finlayson (2004) depict the detected concentrations in the environment and the lethal concentration, 50% (LC50) values (mg/L) for larval delta smelt, fathead minnow, and Sacramento splittail.

**Table D-28. Summary of Toxicity Testing for Invasive Species Herbicides**

| Herbicides and Surfactant | Highest Detected Concentration (mg/L) | Delta Smelt LC50 (mg/L) | Fathead Minnow LC50 (mg/L) | Sacramento Splittail LC50 (mg/L) |
|---|---|---|---|---|
| Weedar 64® (2,4-D) | 0.260 | 149 | 216 | 446 |
| Rodeo® (glyphosate) | 0.037 | 270 | 1,154 | 1,132 |
| R-11® (NP & NPE) | 0.167 | 0.7 | 1.1 | 3.9 |
| Sonar® (fluridone) | 0.012 | 6.1 | 5.7 | 4.8 |
| Reward® (diquat) | 0.110 | 1.1 | 0.43 | 3.7 |
| LC50 = lethal concentration, 50%. | | | | |

Rodeo®, Weedar 64®, and Sonar® 96-h LC50 values for the three fish species are several orders of magnitude higher than detected concentrations in the environment and would not be expected to cause lethal or sublethal effects in larval fish (Riley and Finlayson 2004). However, the LC50 values for Reward®, and R-11® are lower and approach the levels found in the environment, with the highest concentrations being above the LC50 values for both fathead minnow and splittail larvae (Riley and Finlayson 2004). However, these levels were reduced to background levels within 24 hours of application (Anderson 2003). R-11® is a surfactant used with both Rodeo® and Weedar 64®. R-11 was virtually undetected in the environment and can be controlled by careful application on plant surfaces only (Riley and Finlayson 2004). In conclusion, it is unlikely that acute toxicity would occur with the application of herbicides, with the possible exception of Reward®. Exposure levels are less than acute toxic levels, and the chemicals have short lives in the environment. Sonar®



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should be examined more closely because of its longer persistence in the environment and application procedures that require repeated treatments in the same area (Riley and Finlayson 2004).

### D.5.7.4 Endocrine Disruptors—Environmental Fate and Transport

EDCs can interfere with the hormonal system in fish at extremely low (ng/L) concentrations, resulting in negative effects on reproduction and development (Bennett et al. 2008; Riordan and Biales 2008; Lavado et al. 2009). Implications for Delta fish communities include changes in population distributions (e.g., changes in sex ratios that may affect population dynamics) that may be contributing to the POD (Brander and Cherr 2010).

Major sources of EDCs in the Central Valley are thought to be pyrethroid pesticides from urban runoff (Oros and Werner 2005; Weston and State Water Resources Control Board 2010), WWTPs (Routledge et al. 1998), and rangelands (Kolodziej and Sedlak 2007). EDCs also include steroid hormones (such as ethinylestradiol, 17β-estradiol, and estrone), plant constituents, plasticizers, and other industrial by-products. Pyrethroids have been documented to pass through secondary treatment systems at municipal WWTPs at concentrations that are toxic to aquatic life, and still may be present in detectable concentrations following tertiary treatment (Weston and State Water Resources Control Board 2010). Runoff from manure-treated fields and rangelands where livestock have direct access to surface waters can result in introduction of excreted endogenous steroid hormones, including estrogens, androgens, and progestins (Kolodziej and Sedlak 2007). Cultivated fields may contribute naturally occurring estrogenic compounds, such as mycotoxins, and some agricultural pesticides and wetting agents (non-ionic detergents) can be converted to estrogenic compounds in the environment or in the liver.

Estrogenic activity is a measurement of the effects of EDCs in the environment; however, this measure does not provide information on the causative substances. Documenting presence of multiple EDCs in surface waters does not necessarily indicate the constituent(s) responsible for adverse effects on fish populations. For example, Lavado with others (2010) conducted a survey of surface waters from 16 locations in California that were analyzed for EDCs using bioassays (which indicate levels of estradiol equivalents [EEQs]) and analysis for steroid hormones, detergent metabolites, agrichemicals, and other anthropogenic contaminants indicative of pharmaceuticals and personal care products. Samples from two of the 16 survey locations with estrogenic activity identified were subjected to bioassay-directed fractionation to try to identify the contaminants responsible for the estrogenic activity. Results were inconclusive.

### D.5.7.5 Endocrine Disruptors—Effects of Preliminary Proposal Conservation Measures

#### D.5.7.5.1 Water Operations

Endocrine disruptors are a diverse group of chemicals, and it is not possible to evaluate fully the potential effects on the distribution and bioavailability of these chemicals from preliminary proposal water operations.



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#### D.5.7.5.2 Restoration

Given current knowledge, there is potential for endocrine disruptors associated with pesticides to be present in ROA soils and mobilized by inundation of ROAs. Because the chemical characteristics of this group are diverse, the compounds may become mobilized and more bioavailable as suspended particulates in the water column, or in the dissolved phase in the water column. The type of endocrine disruptors and the possibility of mobilization would need to be evaluated on a site-specific basis, taking into consideration the types of pesticides historically used on the property.

## D.5.8 Other Urban Contaminants

Development accounts for only 8% of land area in the Delta, but urban sources, and specifically WWTPs, have been identified as important sources of some toxins (see discussion of pyrethroids and ammonia in previous sections).

The primary Delta urban centers are located in both the Sacramento River watershed (cities of Sacramento and West Sacramento) and the San Joaquin River watershed (city of Stockton). Lead, PCBs, and hydrocarbons (typically oil and grease) are common urban contaminants that are introduced to aquatic systems via nonpoint-source stormwater drainage, industrial discharges, and municipal wastewater discharges. Lead, PCBs, and oil and grease all tend to adhere to soils, although some lighter components of oil and grease can become dissolved in water. Because they adhere to particulates, they tend to settle out close to the source and likely will be found at highest concentrations adjacent to the urban areas. PCBs are very persistent, adsorb to soil and organics, and bioaccumulate in the food chain. Lead also will adhere to particulates and organics but does not bioaccumulate at the same rate as PCBs. Hydrocarbons will biodegrade over time in an aqueous environment and do not tend to bioaccumulate; thus, they are not persistent.

Lead and hydrocarbons have not been identified on the 303(d) list, and information on their presence and distribution in the Delta is very limited. Thus, they are not considered in this effects analysis. PCBs are listed on the 303(d) list and are discussed below.

### D.5.8.1 Polychlorinated Biphenyls

PCBs were banned in the late 1970s, but because of their persistence in the environment, they are still found in mostly urban soils and sediments. High levels of PCBs in environmental media and fish have been studied extensively in San Francisco Bay, which historically has received large amounts of urban runoff and industrial discharge. Although the north Delta, the Natomas east main drain in Sacramento, and the Stockton Deep Water Ship Channel are listed on the 303d list of impaired waters for PCB contamination (State Water Resources Control Board 2010), few data are available concerning current concentrations or distribution of PCBs in the Delta.

However, studies have not been conducted to evaluate the concentrations or distribution of PCBs in the Delta environment. Fish studies in the Delta have indicated the presence of PCBs in the food chain, but little work has been done in characterizing PCB concentrations in surface water and sediment, and identifying the source of PCBs. Because PCBs biomagnify through the food chain, and many of the larger fish migrate through the San Francisco estuary, including the Delta, the location of the PCB source cannot be identified through fish tissue analysis.

A study of largemouth bass from the Sacramento River demonstrated significantly higher levels of PCBs in eggs from the river compared to hatchery-raised fish (Ostrach et al. 2008). Elevated

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concentrations of PCBs were reported in tissues of fish near Stockton (Lee et al. 2002; Davis et al. 2000). Studies by deVlaming (2008) and Davis with others (2000) reveal that PCB concentrations in fish tissue samples from the north Delta and the Stockton Deep Water Ship Channel exceeded thresholds for human health. deVlaming's 2005 fish tissue composite samples also found elevated PCB concentrations in the Mokelumne and Tuolumne Rivers. However, deVlaming points out that, as lipophilic legacy contaminants, PCBs are expected to be found in higher concentrations in older, fattier fish, such as those that were sampled. The Sacramento sucker consistently had the highest PCB concentrations in these studies but should not be considered an appropriate model for other species because of its high lipid content (deVlaming 2008).

Overall, deVlaming found that the results from the 2005 tissue samples indicate that while high concentrations of PCBs can be found in older, fattier fish in specific regions of the Delta (north Delta, Sacramento, and Stockton), Delta PCB concentrations are generally below Office of Environmental Health Hazard Assessment (OEHHA) screening values. In addition, deVlaming suggests that his 2005 results indicate that the north Delta may be eligible for 303d de-listing. Similarly, the 2008 TMDL for PCBs in San Francisco Bay states that PCBs in the Delta are expected to attenuate naturally, thus eliminating the need for implementing action to reduce PCBs in Delta waters. Based on the information presented here, PCBs are not expected to be affected by preliminary proposal actions.

## D.6 Effects of Changes in Toxins on Covered Fish Species

### D.6.1 Summary of Conclusions

The preliminary proposal involves substantial restoration that would be implemented throughout the Delta over the 50-year implementation period as well as changes in water operations that could change how some toxins move through the Delta. As discussed in previous sections of this appendix, and further below, few to no effects on toxins in the Delta are expected from preliminary proposal water operations. Restoration of land with metals and pesticides in soils that could be mobilized into the aquatic system when inundated is expected to increase the bioavailability of some toxins to covered fish species. Given the current understanding of the complex processes involved in mobilizing these toxins, it cannot be modeled or estimated with any confidence. This appendix provides a full conceptual framework to understand the relevant processes. Site-specific analyses of restoration areas will be required to estimate the magnitude of the effects. Important to this picture is that taking lands out of agricultural use will result in an overall reduction of agriculture-related toxin loading, including pesticides, copper, and in some cases, concentrated selenium in irrigation drainage.

In general, the following conclusions can be drawn.

- Preliminary proposal water operations will have few to no effects on toxins in the Delta.
- Preliminary proposal restoration will increase bioavailability of certain toxins, especially methylmercury, but the overall effects on covered fish species are expected to be localized and of low magnitude.
- Available data suggest that species exposure to toxins would be below sublethal and lethal levels.



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- The long-term benefits of restoration will reduce exposure to existing toxins in the environment and eliminate sources.

The following sections provide additional detail on the specific effects of toxic constituents on covered fish species.

## D.6.2 Conclusion of Effects of Toxins on Covered Fish Species

Effects on covered fish species will depend on the species/life stage present in the area of elevated toxins and the duration of exposure. Release of toxic constituents from sediments (e.g., in restored areas) is tied to inundation, and so highest concentrations will occur during seasonal high water and to a lesser extent for short time periods on a tidal cycle in marshes. A full description of fish occurrence over the species' life cycle is included in Appendix A and is integrated into the following sections where appropriate.

### D.6.2.1 Mercury

Model results presented in Section D.5.1.2.1 indicate that preliminary proposal water operations will not adversely affect covered fish species. However, BDCP restoration efforts have the potential to increase the exposure of fish to methylmercury mobilized during inundation of restored tidal wetlands and floodplains, which are used for rearing by covered fish species. The areas expected to have the highest potential for methylmercury are the Yolo Bypass and, to a lesser extent, the Mokelumne-Cosumnes River. The amounts of methylmercury mobilized and resultant effects on covered fish species are not currently quantifiable. Slotton and others (2000: 43) noted:

> Results to date suggest that wetlands restoration projects may result in localized mercury bioaccumulation at levels similar to, but not necessarily greater than, general levels within their surrounding Delta subregion. Nevertheless, high methylation potential, flooded wetland habitat may be the primary source of methyl mercury production in the overall system...Careful monitoring will be essential to assess the actual effects of new wetlands restoration projects.

Also, Slotton and others (2000) have noted that inland silversides from areas adjacent to flooded Delta tracts similar to proposed restoration sites did not exhibit elevated methylmercury.

The following discussion is based on the assumption that some level of methylmercury will be mobilized at BDCP ROAs. It also should be noted that a methylmercury mitigation conservation measure is part of the BDCP, and requires integration of design elements into restoration projects to decrease methylmercury production.

#### D.6.2.1.1 Eggs

The direct exposure of salmonid, sturgeon, and lamprey eggs to increased levels of methylmercury as a result of the preliminary proposal would not occur because salmonid, sturgeon, and lamprey eggs are not present anywhere that restoration is proposed. It is possible that maternal transfer could occur, i.e., prespawned eggs could be exposed to methylmercury from adult consumption of contaminated prey. Splittail, delta smelt, and longfin smelt all spawn in or near areas that would be restored under the preliminary proposal and therefore have the potential for increased exposure to methylmercury. For delta smelt and longfin smelt that spawn directly downstream of the Yolo Bypass or other ROAs in the west or north Delta, exposure of the eggs to aqueous mercury could range from 9 to 14 days (delta smelt) and up to 40 days (longfin smelt). Exposure of splittail eggs would be even less, with eggs hatching in 3–7 days. It is not known what level of mercury would be



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assimilated and transferred to the larvae. Mercury exposure in eggs can lead to egg failure and developmental effects, but the levels of mercury that would have these results are not fully understood.

#### D.6.2.1.2 Larvae and Juveniles

Effects of increased methylmercury are expected to be minimal for fish rearing in the Delta. Henery and others (2010) compared methylmercury in Chinook salmon confined in the Yolo Bypass with those from the Sacramento River and found that the fish that reared in the Yolo Bypass accumulated 3.2% more methylmercury than fish held in the nearby Sacramento River. However, it should be noted that the mean methylmercury concentration for fish in the floodplain was 0.0567 µg/g and only two of the 199 individuals sampled had greater than 0.20 µg/g tissue methylmercury (a whole-body threshold of potential importance for sublethal effects on fish for growth, reproduction, development, and behavior) (Beckvar et al. 2005 as cited by Henery et al. 2010: 561). In addition, the 3.2% increase observed should be considered in the context of the life stage, i.e., the fish would subsequently be leaving the Plan Area and therefore no longer would be exposed to elevated concentrations of mercury, while also growing considerably larger in the ocean and therefore diluting accumulated mercury in their increasing body mass.

Henery also found that the body mass of free-ranging Chinook salmon that reared in the floodplain grew at a rate of 3.5% per day, compared to 2.8% per day for Chinook salmon that reared in the adjacent Sacramento River. Therefore, it appears that the increased exposure to methylmercury in rearing salmonids generally would not be high enough to elicit measurable sublethal effects. This growth dilution effect would be even more pronounced in adult fish that grow to three orders of magnitude larger over their life span, making the amount of methylmercury tissue accumulation as a juvenile insignificant (Henery et al. 2010).

Unlike salmonids, juvenile and subadult green and white sturgeon spend considerable time in the Delta. Laboratory studies have shown that high concentrations of methylmercury (25–50 ppm) in sturgeon diet are required to elicit any sort of adverse effect (Kaufman pers. comm.; Lee et al. 2011). Such elevated levels of methylmercury would not be experienced in the preliminary proposal restoration areas or the Yolo Bypass. Although juvenile sturgeon spend more time than any other covered fish species in the Plan Area, they also have the fastest growth rate of any species. Accumulation of methylmercury in the body tissue thus is mediated by growth dilution from the rapidly increasing muscle mass (Kaufman pers. comm.). Total body burden of methylmercury may increase, but tissue concentration of methylmercury would be expected to remain relatively constant (Kaufman pers. comm.) Juvenile sturgeon are primarily benthivores, feeding mostly on secondary productivity in the food chain (small crustaceans, clams, etc.) and therefore would not bioaccumulate mercury as fast as a top predator.

Larvae and juvenile splittail, delta smelt, and longfin smelt feed very low on the food chain and, similar to sturgeon juveniles described above, would bioaccumulate methylmercury at low levels. Additionally, juvenile longfin smelt occur primarily in San Pablo Bay and San Francisco Bay where no restoration or effects from water operations related to the preliminary proposal would occur. Similarly, juvenile delta smelt occur primarily in the west Delta and Suisun Bay, where elevated levels of methylmercury from restoration are not likely, and in Suisun Marsh, where the potential for elevated methylmercury is also low. However, juvenile smelt remaining in the north Delta area would experience exposure from food in the Yolo Bypass and Cache Slough regions.



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#### D.6.2.1.3 Adults

Central Valley adult salmonids do not feed during their time in the Delta (Sasaki 1966) and potentially would be exposed to the elevated methylmercury produced in this portion of the Delta through absorption from water through their gills. Additionally, they tend to stay in the main channels through the Delta, rather than the shallow, slow-moving waters of wetlands and floodplains. As a result of their limited time in the estuary and the tendency to migrate in the main channels, adult salmonids are not likely to be exposed to a significantly different quantity of methylmercury under the preliminary proposal than under current conditions. Elevated mercury levels in the East Delta subregion could be encountered at the confluence of the Mokelumne and Cosumnes Rivers, although the number of spawning occurrences in this area by covered fish species is relatively small.

Adult sturgeon would be using the preliminary proposal regions primarily as a pathway for spawning migration, although they do forage in the lowest preliminary proposal regions. Adult sturgeon would not accumulate high tissue loads of methylmercury for the same reason as the juveniles, coupled with the fact that they spend little time in areas that are projected to have increased methylmercury production. Analyses of white sturgeon from San Francisco Bay (albeit downstream of the Plan Area) found median mercury concentration in muscle below the screening level for human consumption concern of 0.3 µg/g wet weight (Greenfield et al. 2000).

Although adult life stages of splittail, delta smelt, and longfin smelt feed and spawn in areas with potential for elevated methylmercury levels, they feed primarily on lower trophic level food sources and therefore do not accumulate methylmercury at rates as high as if they preyed on fish. Additionally, they are not expected to spend excessive amounts of time in these areas, so the uptake through their gills and food is expected to be minimal. Nevertheless, delta smelt have been shown to accumulate appreciable quantities of mercury: Bennett and coauthors (2001) found average levels of 0.18 µg/g, which is just under the 0.20 µg/g general threshold for effects on fish suggested by Beckvar and coauthors (2005 as cited by Henery et al. 2010: 561). There is no evidence for acute toxicity of mercury being related to recent declines of pelagic fish such as delta smelt and longfin smelt, although mercury, selenium, and copper may have had a chronic effect on these species (Brooks et al. 2011).

### D.6.2.2 Selenium

As discussed in Section D.5.2, elevated selenium is recognized as a threat to fish in the Delta. However, few to no effects on selenium from preliminary proposal actions have been identified. Historically, the San Joaquin River has been a major source of selenium to the Delta; however, the selenium source is being addressed and selenium concentrations are decreasing. Further, modeling results indicate that preliminary proposal water operations would have few to no effects on selenium concentrations in water or fish tissue. Suisun Marsh has high levels of selenium in filter-feeding clams that bioaccumulate selenium and form the base of the food chain, which results in biomagnification to covered fish species. However, no mechanisms for the preliminary proposal actions to increase selenium in Suisun Marsh have been identified.

As a conservative approach, the following discussion of the possible effects of preliminary proposal actions on selenium in covered fish species assumes that some increase in selenium will occur under the preliminary proposal actions. Any increases are expected to be localized and associated with



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inundation of ROAs, mainly in the south Delta, which receives input from the San Joaquin River, a historical source of selenium.

The bioaccumulation and effects of selenium on fish have much to do with their feeding behavior. The overbite clam, *C. amurensis*, accumulates selenium and is key to mobilizing it into the food chain. It is abundant in Suisun Bay, but the preliminary proposal is not expected to increase the contribution of selenium to this area given the distance from the San Joaquin River source (modeling results corroborate). Smelt, steelhead, and Chinook salmon would be expected to have low exposure to selenium as they are feeding on pelagic organisms that are able to excrete selenium at more than 10 times the rate of the benthic clam, *C. amurensis*. This is in contrast to sturgeon and splittail that are at risk for teratogenesis because of their diet preference for *C. amurenis*, and high concentrations of selenium bioaccumulated in their tissues, especially reproductive organs, liver, and kidneys. Deformities occur in developing embryos when selenium replaces sulfur in sulfur-rich hard tissues (Diplock 1976). For example, recent field surveys identified Sacramento splittail from Suisun Bay (where selenium concentrations are highest) that have deformities typical of selenium exposure (Stewart 2004). Both green and white sturgeon feed on *C. amurensis* in the three lower subregions (Suisun Bay, Suisun Marsh, and West Delta) but are not likely to be affected by the preliminary proposal–related changes in selenium because of the distance from the source area (Grassland in San Joaquin River basin). Modeling results corroborate this conclusion. Little is known about lampreys, but based on lamprey ammocoete occurrence in the Delta (mostly in the Sacramento River area), it is expected that their exposure to selenium-laden sediments and water would be minimal.

#### D.6.2.3 Copper

Copper will be present in agricultural soils and could be mobilized by inundation of the ROAs, as it is fairly immobile in soils, but is very mobile in an aquatic system. Preliminary proposal water operations are not expected to have much effect on copper concentrations, although there is a slight chance of mobilization of copper from increased flow at the weir at the upstream end of the Yolo Bypass, where copper concentrations may be elevated.

Mobilized copper could have a temporary adverse effect on juvenile fish, namely salmonids, splittail, and smelt that rear in the Yolo Bypass. Additionally, splittail adults, eggs, and larvae may be exposed while in the bypass. Likewise, rearing juvenile and adult salmonids and sturgeon may be exposed in other ROAs previously used for agriculture.

It is difficult to establish precise concentrations at which copper is acutely toxic to fish, as a large number of water chemistry parameters (including temperature, pH, DOC, and ions) can affect the bioavailability of copper to the fish population (U.S. Environmental Protection Agency 2007). As discussed in Section D.5.3, copper is present in the Sacramento River at low concentrations (2 µg/L). Connon with others (2010) demonstrated that the median lethal concentration of dissolved copper at which 10% of delta smelt juveniles died after 7 days of exposure under experimental conditions (LC10) was 9.0 µg/L; 50% of juveniles died (LC50) when exposed to a median concentration of 17.8 µg/L. Although 96-hour larval delta smelt mortality suggested higher concentrations than juveniles (median LC10 = 9.3 µg/L; median LC50 = 80.4 µg/L), these results were complicated by differences in exposure duration and experimental conditions (particularly for factors such as temperature and conductivity that may affect copper toxicity) (Connon et al. 2010).



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Carreau and Pyle (2005) demonstrated that copper exposure during embryonic development of fathead minnows could result in permanent impairment of chemosensory functions but that the same exposure caused only temporary impairment in adults once copper is removed, suggesting that the specific life stage at the time of exposure also plays a role in the toxicity of copper to fish. Baldwin and coauthors (2003) reported inhibition of olfactory physiology in salmonids at concentrations of 6 µg/L (background plus spiked concentration), indicating that low levels of copper over a short period of exposure could affect migratory ability in salmonids. Sandahl (2007) reported impairment of sensory functions and avoidance behavior in juvenile coho at copper concentrations of 2µg/L. There is some evidence that larval delta smelt swimming velocity decreases as dissolved copper concentration increases, although experimental testing did not find statistical differences between test subjects and controls (Connon et al. 2010). Various delta smelt genes have been to shown to have altered expression in copper-exposed larvae (Connon et al. 2010).

Localized, short-term increases in copper concentrations are possible near ROA areas, but the length of time and the concentrations cannot be determined with available data. Overall, because copper concentrations are generally low in Delta waters, preliminary proposal actions are not expected to result in increased effects of copper on covered fish species. In fact, halting agricultural use and application of pesticides on restoration areas will result in decreased loading of copper to the Delta system and will provide a long-term net benefit to the ecosystem.

### D.6.2.4 Ammonia

Based on the analysis presented in Section D.5.4, preliminary proposal actions are not expected to result in substantial increases in ammonia concentrations in the aquatic system that could affect covered fish species. Analysis of the ability of the Sacramento River to dilute ammonia discharges from the Sacramento WWTP indicates that resultant concentrations would be within ecologically acceptable limits under the preliminary proposal. Further, no addition or mobilization of ammonia to the aquatic system would result from restoration activities.

### D.6.2.5 Pyrethroids, Organophosphate Pesticides, and Organochlorine Pesticides

Based on the analyses in Sections D.5.5, D.5.6, and D.5.7, changes in concentrations of pyrethroids, organophosphate pesticides, and organochlorine pesticides resulting from the preliminary proposal are expected in the vicinity of agricultural land restored to marshes and floodplains. These chemicals either have a strong affinity for sediment and will settle out of the water column, or readily degrade in an aquatic system. Thus, it is expected that increases in concentrations due to preliminary proposal actions will be of relatively short duration and localized near ROAs. Specific areas of these elevated toxins have not been identified, but they can be expected in any of the ROAs. Preliminary proposal restoration will take these agricultural areas out of production, therefore eliminating the source and reducing these chemicals in the Delta system, providing a long-term ecological benefit.

Pyrethroids have been shown to be lethal as low as 1 µg/L, although there are many different chemicals in this group with varying toxicities for fish. Likewise, little is known on the effects of organophosphates on fish, but elevated concentrations of organophosphates are more likely to affect the lower trophic levels that the covered fish species prey on than the fish directly (Turner 2002). As these pesticides are neurotoxins, behavioral effects are of primary concern; however, Scholz (2000) points out that the effects are not well understood. Scholz (2000) found that diazinon



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concentrations as low as 1 µg/L resulted in significant impairment of predator-alarm responses, and slightly higher concentrations of 10 µg/L caused the impairment of homing behavior in Chinook salmon. Organochlorine pesticides are neurotoxic, are likely carcinogenic, and have been implicated as endocrine disruptors because of their estrogenic nature and effects on reproductive development (Leatherbarrow et al. 2006). These pesticides are highly persistent and lipophilic, and as such, they strongly bioaccumulate (Werner et al. 2008). Because of their persistence in the environment and biomagnifications through the foodweb, the main concern with organochlorines is bioaccumulation in the higher trophic levels and implications for human consumption. However, organochlorine pesticides and degradation products can directly affect fish through toxicity to lower-level invertebrates on the food chain, and toxicity to small and early life stage fish, but there is little information specific to effects on individual species. Sublethal effects may include reproductive failure and behavioral changes. Ostrach's (2009) report suggests that largemouth bass have been experiencing reproductive failure due to organochlorine compounds in San Francisco Bay, which is likely due to concentrations accumulated through biomagnifications. Because they tend to adhere to soils and particulates, organochlorine compounds may take longer to flush out than some of the more environmentally mobile constituents discussed above (e.g., copper).

In the Delta, fish in higher trophic levels are particularly vulnerable to these pesticides, as the chemicals will biomagnify and bioaccumulate in their tissues. These fish include white and green sturgeon, salmonids, and lampreys. As smaller fish at lower trophic levels, smelt and splittail can be expected to have less biomagnification of these pesticides.

More detailed analysis of pyrethroid, organophosphate pesticide, and organochlorine pesticide effects would require site-specific information, but overall the preliminary proposal is not expected to substantially increase the potential exposure of fish because elevated bioavailability likely would be localized near ROAs and over a relatively short time period. Additionally, restoration of agricultural land will result in an overall reduction in these chemicals in the Delta system, with an overall net ecological benefit.

### D.6.3 Uncertainties and Information Needs

As discussed throughout this appendix, the amount of toxins that will be mobilized and made more bioavailable to covered fish species due to inundation of ROAs is uncertain. This uncertainty is most critical for methylmercury, and to a lesser extent for pesticides and other metals. For each of the toxins, the chemical-specific and site-specific factors that will determine resultant effects vary. Conservation CM12 is included in the BDCP to support site specific evaluation and monitoring of methylmercury production in restored areas. Data from this monitoring will assist in evaluating the effects of restoration actions and reduce the uncertainty associated with the potential exposure of covered fish to methylmercury mobilized by these actions.

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## *No comments*

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***No comments***

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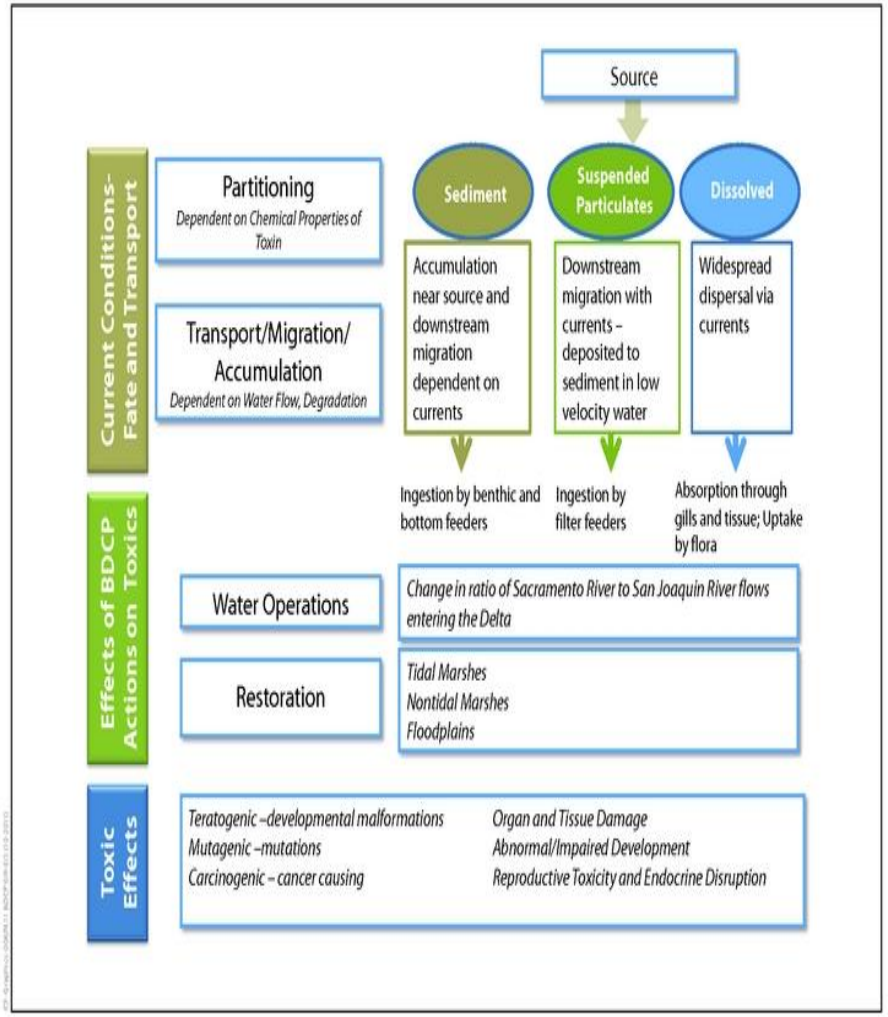


**Figure D-1**
**Generic Conceptual Model to Evaluate BDCP Toxins Effects**

***No comments***

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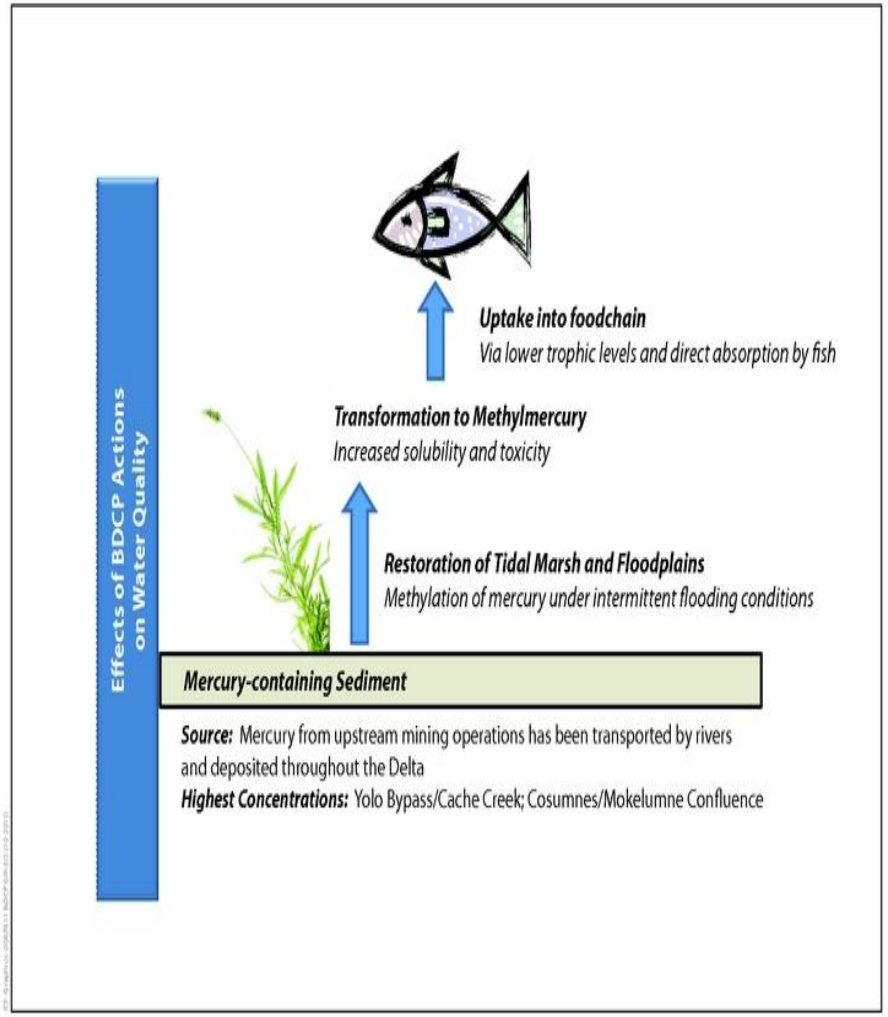


**Figure D-2**
**Methylmercury Cycling in an Aqueous System**

***No comments***

- n/a -

Attachment 4.A

# Bioaccumulation Model Development for Mercury Concentrations in Fish

## 4.A.1 Introduction

Areas of enhanced bioavailability and toxicity of mercury (created through the mercury methylation process) exist in the Sacramento–San Joaquin River Delta (Delta), and elevated mercury concentrations in fish tissue produce estimates of exposure and risk to humans and wildlife. Consequently, the beneficial uses most directly affected by mercury are shellfish harvesting and commercial and sport fishing activities that pose a human health concern, and wildlife habitat and rare, threatened, and endangered species resources that can be exposed to bioaccumulation of mercury. Because of these concerns, mercury was the first total maximum daily load (TMDL) approved for San Francisco Bay in 2007 (San Francisco Bay Regional Water Quality Control Board 2006), and a methylmercury TMDL is in progress for the Delta (Central Valley Regional Water Quality Control Board 2008). The Delta and Suisun Marsh both are listed as impaired water bodies on the Clean Water Act Section 303(d) lists for mercury in fish tissue (State Water Resources Control Board 2007).

The conceptual model of mercury transport, fate, and risk for the Delta as used in this study shows important linkages among waterborne loading, waterborne concentrations, and water, sediment, and biotic processing of mercury and methylmercury. Mercury is strongly particle-associated and tends to settle and accumulate in sediment deposition areas that facilitate mercury methylation by sulfur-reducing bacteria. From that point in the cycle, diet (rather than waterborne concentration) is the primary route for methylmercury exposure to fish, wildlife, and humans.

Mercury in largemouth bass was chosen as the representative measure of fish bioaccumulation for this study because bass tissue concentrations have been described recently over a wide area of the Delta. Consequently, the fish tissue concentrations of mercury could be linked in time and space with estimated waterborne concentrations of mercury and methylmercury to examine possible causal linkages. In addition, the California Regional Water Quality Control Board, Central Valley Region (Central Valley Water Board) already successfully used this general approach to link waterborne and largemouth bass mercury concentrations for broad areas of the Delta. However, for the preliminary proposal, it was desirable to examine fish tissue–water mercury linkages at defined locations rather than general Delta conditions over broad areas.

## 4.A.2 Mercury Concentrations in Water and Fish

The DSM2 output locations where whole-body largemouth bass data for mercury were available are shown on Table D.A-1 (tables are at the end of this attachment). The geometric mean mercury and methylmercury concentrations in water were estimated for selected DSM2 output locations and then used to estimate mercury concentrations in fish tissue (fillets).

The quarterly and annual average waterborne mercury and methylmercury concentrations for the DSM2 output locations are shown in Table D.A-1 (for Year 2000). Note that the first quarter DSM2



***No comments***

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model results were discarded because the model "ramps up" for a new year, and the average values from those first months were distinctly lower than for the other quarters. Therefore, the annual average for the year was computed from the last three quarters.

Largemouth bass were chosen for modeling because they are popular sport fish, top predators, live for several years, and tend to stay in the same area (that is, they exhibit high site-fidelity). Consequently, they are excellent indicators of long-term average mercury exposure, risk, and spatial pattern for both ecological and human health. Fish tissue concentrations were available from 1999 and 2000 at modeled locations; DSM2 estimated waterborne concentrations from those locations were modeled on the year 2000 hydrology. The Sacramento River inflows and Cosumnes River were the areas of highest fish tissue bioaccumulation of mercury. Bass had uniformly lower tissue concentrations in the central Delta. The Central Valley Water Board TMDL tissue concentration goal for normalized 350-mm total length largemouth bass tissue is 0.24 mg/kg wet weight (ww) mercury for the Delta (Central Valley Regional Water Quality Control Board 2008).

## 4.A.3 Bioaccumulation Model Predicting Mercury in Fish

The largemouth bass tissue mercury concentrations were presented as edible fillet concentrations for fish normalized to 350 mm in total length as supplied directly by San Francisco Estuary Institute (SFEI) (2010). It is important to standardize concentrations to the same size fish at each location because of the well-established positive relationship between fish size and age and tissue mercury concentrations (Alpers et al. 2008).

Co-located fish fillet mercury concentrations were graphed against their corresponding values of waterborne mercury or methylmercury in standard, linear regression analyses using annual average and quarterly water values calculated using the SAS Institute's Statview 5 analytic software (SAS Institute 1998). The data were log-transformed to improve normality. The positive relationships with mercury were not as strong as with methylmercury. The best choice for a predictive model was the linear regression showing a statistically significant relationship between annual average waterborne methylmercury concentrations in water from the third quarter of the year and largemouth bass tissue mercury concentrations:

Fish mercury (mg/kg ww) = 10^(4.217+ (Log methylmercury in water, µg/L × 1.164)) **[Eq.1]**

The results of this regression model in can be compared to those using the alternative from the Central Valley Water Board TMDL model, which also predicts 350-mm normalized largemouth bass fillets from methylmercury in water. This comparison is shown in Table D.A-2. The Central Valley Water Board developed a model based on largemouth bass as grouped in major areas of the Delta compared to average methylmercury concentrations in water for those areas (Central Valley Regional Water Quality Control Board 2008):

Fish mercury (mg/kg ww) = 20.365 × ((methylmercury in water, ng/L)^1.6374) **[Eq. 2]**

For the DSM2-estimated water concentrations for 2000, the Central Valley Water Board model consistently overpredicted the fish concentrations as compared to the regression model (mean of 0.719 mg/kg compared to 0.411 mg/kg) relative to the measured value of 0.446 mg/kg (Table D.A-2). For this reason, the regression model was used to predict bass fillet concentrations for this study. The Central Valley Water Board TMDL model was not established to predict fish tissue



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concentrations but to provide the linkage between the 0.24 mg/kg tissue mercury TMDL target and the waterborne goal of 0.066 ng methylmercury/L.

## 4.A.4 References

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State Water Resources Control Board. 2007. *2006 CWA Section 303(d) List of Water Quality Limited Segments.* Sacramento, CA. Available: <http://www.waterboards.ca.gov/water_issues/programs/tmdl/docs/303dlists2006/epa/state_usepa_combined.pdf >. Accessed: March 12, 2009.

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***No comments***

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2 **Table D.A-1. Mercury and Methylmercury Concentration Estimates in Water at Selected Locations in the Delta**

| | Concentration (µg/L) | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | Second Quarter* | | Third Quarter | | Fourth Quarter | | Annual Average | |
| DSM2 Output Location | Hg | MeHg | Hg | MeHg | Hg | MeHg | Hg | MeHg |
| Sacramento River RM 44 | 0.00410 | 0.00010 | 0.00410 | 0.00010 | 0.00410 | 0.00010 | 0.00410 | 0.00010 |
| Mokelumne River downstream of Cosumnes | 0.00856 | 0.00022 | 0.00845 | 0.00022 | 0.00855 | 0.00022 | 0.00852 | 0.00022 |
| Cosumnes River | 0.00860 | 0.00022 | 0.00860 | 0.00022 | 0.00860 | 0.00022 | 0.00860 | 0.00022 |
| Cache Slough | 0.00411 | 0.00010 | 0.00413 | 0.00010 | 0.00412 | 0.00010 | 0.00412 | 0.00010 |
| Sacramento River at Isleton | 0.00410 | 0.00010 | 0.00411 | 0.00010 | 0.00411 | 0.00010 | 0.00411 | 0.00010 |
| San Joaquin River Potato Slough | 0.00532 | 0.00013 | 0.00420 | 0.00010 | 0.00424 | 0.00010 | 0.00459 | 0.00011 |
| Sherman Island | 0.00479 | 0.00011 | 0.00450 | 0.00010 | 0.00475 | 0.00009 | 0.00468 | 0.00010 |
| White Slough downstream of Disappointment Slough | 0.00686 | 0.00016 | 0.00466 | 0.00012 | 0.00490 | 0.00013 | 0.00547 | 0.00014 |
| Franks Tract | 0.00546 | 0.00013 | 0.00426 | 0.00011 | 0.00429 | 0.00010 | 0.00467 | 0.00011 |
| Big Break | 0.00493 | 0.00012 | 0.00436 | 0.00010 | 0.00448 | 0.00010 | 0.00459 | 0.00011 |
| Mildred Island | 0.00699 | 0.00015 | 0.00461 | 0.00012 | 0.00509 | 0.00012 | 0.00556 | 0.00013 |
| San Joaquin River Naval Station | 0.00762 | 0.00016 | 0.00763 | 0.00016 | 0.00761 | 0.00015 | 0.00762 | 0.00016 |

Notes:
*First quarter DSM2 modeled water concentrations were not used because of model "ramp up" artifacts.
MeHg = methylmercury.
Hg = mercury.
RM = river mile.

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**Table D.A-2. Modeled and Measured Bass Fillet Mercury Concentrations**

| Site | Bass Tissue Concentration (mg/kg ww) | | |
|---|---|---|---|
| | Measured Fish | Regression Model | Central Valley Water Board TMDL Model |
| Sacramento River RM 44 | 0.869 | 0.364 | 0.470 |
| Mokelumne River downstream of Cosumnes | 1.091 | 0.930 | 1.758 |
| Cosumnes River | 0.895 | 0.926 | 1.745 |
| Cache Slough | 0.559 | 0.372 | 0.484 |
| Sacramento River at Isleton | 0.628 | 0.366 | 0.473 |
| San Joaquin River Potato Slough | 0.365 | 0.413 | 0.560 |
| Sherman Island | 0.323 | 0.371 | 0.482 |
| White Slough downstream of Disappointment Slough | 0.226 | 0.525 | 0.785 |
| Franks Tract | 0.265 | 0.420 | 0.574 |
| Big Break | 0.226 | 0.390 | 0.518 |
| Mildred Island | 0.226 | 0.498 | 0.729 |
| San Joaquin River Naval Station | 0.352 | 0.621 | 0.996 |
| San Joaquin River Vernalis | 0.739 | 0.583 | 0.912 |
| **Geometric mean** | **0.446** | **0.493** | **0.719** |
| **Maximum** | **1.091** | **0.930** | **1.758** |
| **Minimum** | **0.226** | **0.364** | **0.470** |
| mg/kg ww = milligram per kilogram wet weight. | | | |

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Attachment 4.B

# Selenium Modeling Methods

## 4.B.1 Bioaccumulation Model Development for Selenium Concentrations in Whole-Body Fish, Bird Eggs, and Fish Fillets

Plan-related changes in waterborne concentrations of selenium in the Sacramento–San Joaquin River Delta (Delta) may result in increased selenium bioaccumulation and/or toxicity to aquatic and semi-aquatic receptors using the Delta. Historical fish tissue data and measured (at Vernalis) or DSM2-modeled (other locations) waterborne selenium concentrations for selected locations in 2000, 2005, and 2007 were used to model water-to-tissue relationships, generally following procedures described by Presser and Luoma (2010).

The output from the DSM2 model (expressed as percent inflow from different sources) was used in combination with the available measured waterborne selenium concentrations to model concentrations of selenium at locations throughout the Delta. These modeled waterborne selenium concentrations were used in the relationship model to estimate bioaccumulation of selenium in whole-body fish and bird eggs. Selenium concentrations in fish fillets then were estimated from those in whole-body fish.

The data and processes used to develop the final models to estimate this selenium bioaccumulation are described in the following sections.

## 4.B.2 Selenium Concentrations in Water

Dissolved selenium data were available for six inflow locations to the Delta. Whole-body largemouth bass data for selenium were available from the following DSM2 output locations.

- Big Break
- Cache Slough at Ryer Island
- Franks Tract
- Knights Landing
- Middle River Bullfrog
- Old River Near Paradise Cut
- Sacramento River Mile (RM) 44
- San Joaquin River Potato Slough
- Vernalis

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The geometric mean selenium concentrations from the inflow locations were combined with the modeled quarterly average percent inflow for each DSM2 output location to estimate waterborne selenium concentrations at selected DSM2 output locations.

The quarterly average mix of water from the six inflow sources was calculated from daily percent inflows provided by the DSM2 model output for the nine DSM2 output locations for which fish data were available. DSM2 data were not available at or near Vietnam Veterans Memorial Bridge on the Sacramento River or Vernalis on the San Joaquin River. Historical data of selenium concentrations in water collected near these locations were used to represent quarterly averages. The geometric mean of total selenium concentrations in water collected from years 2003, 2004, 2007, and 2008 (California Department of Water Resources 2009) at Knights Landing were used to represent quarterly averages of selenium concentrations in water for all years. The geometric means of selenium concentrations (*total* or *dissolved* was not specified) in water collected from years 1999–2007 (Central Valley Regional Water Quality Control Board 2009) were used to represent quarterly averages for all years of selenium concentrations in water at Vernalis.

The quarterly waterborne selenium concentrations at DSM2 locations were calculated using the following equation:

$$C_{water\ quarterly} = \frac{(I_1 \bullet C_1) + (I_2 \bullet C_2) + (I_3 \bullet C_3) + (I_4 \bullet C_4) + (I_5 \bullet C_5) + (I_6 \bullet C_6)}{100} \quad \textbf{[Eq.1]}$$

Where:

$C_{water\ quarterly}$ = quarterly average selenium concentration in water (µg/L) at a DSM2 output location

$I_{1\text{-}6}$ = modeled quarterly inflow from each of the six sources of water to the Delta for each DSM2 output location (percentage)

$C_{1\text{-}6}$ = selenium concentration in water (µg/L) from each of the six inflow sources to the Delta (1-6)

Example Calculation: Modeled Selenium Concentration at Franks Tract Year 2000, First Quarter:

(43.94 [% inflow from Sacramento River water source at Franks Tract] × 0.32 µg/L [Selenium concentration at Sacramento River at Freeport]) + (11.56 [% inflow from East Delta Tributaries water source at Franks Tract] × 0.10 µg/L [Selenium concentration at Mokelumne, Calaveras, and Cosumnes Rivers]) + (15.79 [% inflow from San Joaquin River water source at Franks Tract] × 0.84 µg/L [Selenium concentration at San Joaquin River at Vernalis]) + (0.02 [% inflow from Martinez/Suisun Bay water source at Franks Tract] × 0.09 µg/L [Selenium concentration at San Joaquin River near Mildred Island]) + (0.32 [% inflow from Yolo Bypass water source at Franks Tract] × 0.45 µg/L [Selenium concentration at Sacramento River at Knights Landing]) + (5.06 [% inflow from Delta Agriculture water source at Franks Tract] × 0.11 µg/L [Selenium concentration at Mildred Island, Center])/100 = 0.29 µg/L

The quarterly and average annual waterborne selenium concentrations for the DSM2 output locations were calculated for Year 2000, Year 2005, and Year 2007.

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## 4.B.3 Bioaccumulation of Selenium into Whole-Body Fish and Bird Eggs

Selenium concentrations in whole-body fish and bird eggs were calculated using ecosystem-scale models developed by Presser and Luoma (2010). The models were developed using biogeochemical and physiological factors from laboratory and field studies; information on loading, speciation, and transformation to particulate material; bioavailability; bioaccumulation in invertebrates; and trophic transfer to predators. Important components of the methods included (1) empirically determined environmental partitioning factors between water and particulate material that quantify the effects of dissolved speciation and phase transformation; (2) concentrations of selenium in living and nonliving particulates at the base of the foodweb that determine selenium bioavailability to invertebrates; and (3) selenium biodynamic foodweb transfer factors that quantify the physiological potential for bioaccumulation from particulate matter to consumer organisms and prey to their predators.

### 4.B.3.1 Selenium Concentration in Particulates

Phase transformation reactions from dissolved to particulate selenium are the primary form by which selenium enters the foodweb. Presser and Luoma (2010) used field observations to quantify the relationship between particulate material and dissolved selenium as shown below.

$$C_{particulate} = K_d \bullet C_{water\ column} \quad \textbf{[Eq. 2]}$$

Where:

$C_{particulate}$ = selenium concentration in particulate material (micrograms/kilogram, dry weight [µg/kg dw])

$C_{water\ column}$ = selenium concentration in water column (µg/L)

$K_d$ = particulate/water ratio

The $K_d$ describes the particulate/water ratio at the moment the sample was taken and should not be interpreted as an equilibrium constant (as it sometimes is). It can vary widely among hydrologic environments and potentially among seasons (Presser and Luoma 2010). In addition, other factors such as speciation, residence time, and particle type affect $K_d$. Residence time of selenium is usually the most influential factor on the conditions in the receiving water environment. Short water-residence times (e.g., streams, rivers) limit partitioning of selenium into particulate material. Conversely, longer residence times (e.g., sloughs, lakes, estuaries) allow greater uptake by plants, algae, and microorganisms. Furthermore, environments in downstream portions of a watershed can receive cumulative contributions of upstream recycling in a hydrologic system. Because of its high variability, $K_d$ is a large source of uncertainty in the model, especially if translation of selenium concentration in the water column is necessary.

### 4.B.3.2 Selenium Concentrations in Invertebrates

Species-specific trophic transfer factors (TTFs) for transfer of selenium from particulates to prey and to predators were developed using data from laboratory experiments and field studies (Presser and Luoma 2010). TTFs are species-specific, but the range of TTFs for freshwater invertebrates was found to be similar to TTFs for marine invertebrates determined in laboratory experiments.



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TTFs for estimating selenium concentrations in invertebrates were calculated using the following equation:

$$TTF_{invertebrate} = \frac{C_{invertebrate}}{C_{particulate}}$$

**[Eq. 3]**

Where:

$TTF_{invertebrate}$ = trophic transfer factor from particulate material to invertebrate

$C_{invertebrate}$ = concentration of selenium in invertebrate (µg/g dry weight [dw])

$C_{particulate}$ = concentration of selenium in particulate material (µg/g dw)

A mean aquatic insect TTF was calculated from TTFs for aquatic insect species with similar bioaccumulative potential, including mayfly (Baetidae, Heptageniidae, Ephemerellidae), caddisfly (Rhyacophilidae, Hydropsychidae), crane fly (Tipulidae), stonefly (Perlodidae/Perlidae, Chloroperlidae), damselfly (Coenagrionidae), corixid (*Cenocorixa* spp.), and chironomid (*Chironomus* spp.) aquatic life stages. Species-specific TTFs ranged from 2.14 to 3.2 with a mean TTF of 2.8.

### 4.B.3.3 Selenium Concentrations in Whole-Body Fish

The mechanistic equation for modeling selenium bioaccumulation in fish tissue is similar to that of invertebrates if whole-body concentrations are the endpoint (Presser and Luoma 2010), as follows:

$$TTF_{fish} = \frac{C_{fish}}{C_{invertebrate}}$$

*Where*:

$$C_{invertebrate} = C_{particulate} \bullet TTF_{invertebrate} \quad \textbf{[Eq. 4]}$$

*Therefore*:

$$C_{fish} = C_{particulate} \bullet TTF_{invertebrate} \bullet TTF_{fish}$$

Where:

$C_{fish}$ = concentration of selenium in fish (µg/g dw)

$C_{invertebrate}$ = concentration of selenium in invertebrate (µg/g dw)

$C_{particulate}$ = concentration of selenium in particulate material (µg/g dw)

$TTF_{invertebrate}$ = trophic transfer factor from particulate material to invertebrate

$TTF_{fish}$ = trophic transfer factor from invertebrate to fish

Modeling of bioaccumulation into a particular fish species includes physiology of the organism and its preferred foods. Therefore, variability in fish tissue concentrations of selenium is driven more by

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dietary choices and their respective levels of bioaccumulation (i.e., $TTF_{invertebrate}$) than by differences in the dietary transfer to the fish ($TTF_{fish}$). A diet of mixed prey (including invertebrates or other fish) can be modeled as follows:

$$C_{fish} = TTF_{fish} \bullet \left[ \left( C_1 \bullet F_1 \right) + \left( C_2 \bullet F_2 \right) + \left( C_3 \bullet F_3 \right) \right] \quad \textbf{[Eq. 5]}$$

Where:

$C_{fish}$ = concentration of selenium in fish (µg/g dw)

$TTF_{fish}$ = trophic transfer factor for fish species

$C_{1-3}$ = concentration of selenium in invertebrate or fish prey items 1, 2, and 3 (µg/g dw)

$F_{1-3}$ = fraction of diet composed of prey items 1, 2, and 3

Modeling of selenium concentrations in longer foodwebs with higher trophic levels (e.g., forage fish being consumed by predator fish) can be completed by incorporating additional TTFs; for example:

$$C_{predator\ fish} = TTF_{invertebrate} \bullet C_{particulate} \bullet TTF_{forage\ fish} \bullet TTF_{predator\ fish} \quad \textbf{[Eq. 6]}$$

Where:

$C_{predator\ fish}$ = concentration of selenium in fish (µg/g dw)

$TTF_{invertebrate}$ = trophic transfer factor from particulate material to invertebrate

$C_{particulate}$ = concentration of selenium in particulate material (µg/g dw)

$TTF_{forage\ fish}$ = trophic transfer factor for invertebrates to foraging fish species

$TTF_{predator\ fish}$ = trophic transfer factor for forage fish to predator species

The fish TTFs reported in Presser and Luoma (2010) ranged from 0.5 to 1.6, so the average fish TTF of 1.1 was used for all trophic levels of fish.

Modeled selenium concentrations in whole-body fish were used to estimate selenium concentrations in fish fillets, as described below.

### 4.B.3.4 Selenium Concentrations in Bird Eggs

Selenium concentrations in bird tissues can be estimated, but the transfer of selenium into bird eggs is more meaningful for evaluating reproductive endpoints (Presser and Luoma 2010). Examples of models for selenium transfer to bird eggs are as follows:

$$C_{bird\ egg} = C_{particulate} \bullet TTF_{invertebrate} \bullet TTF_{bird\ egg} \quad \textbf{[Eq. 7]}$$

Or:

$$C_{bird\ egg} = C_{particulate} \bullet TTF_{invertebrate} \bullet TTF_{fish} \bullet TTF_{bird\ egg} \quad \textbf{[Eq. 8]}$$

Where:

$C_{bird\ egg}$ = concentration of selenium in bird egg (µg/g dw)

$C_{particulate}$ = concentration of selenium in particulate material (µg/g dw)

$TTF_{invertebrate}$ = trophic transfer factor from particulate material to invertebrate

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$TTF_{fish}$ = trophic transfer factor from invertebrate to fish

$TTF_{bird\ egg}$ = trophic transfer factor from invertebrate or fish (depending on diet) to bird egg

The only bird TTF presented in Presser and Luoma (2010) was for the mallard ($TTF_{bird\ egg}$ = 1.8). Mallards are considered a species sensitive to selenium based on reproductive endpoints.

## 4.B.4 Refinement of Selenium Bioaccumulation Models for the Delta

Several models were evaluated and refined to estimate selenium uptake in fish and in bird eggs from waters in the Delta. Input parameters to the model ($K_d$s and TTFs) were varied among the models as refinements were made. Rationale for each refinement is presented below with the discussion of each model. In addition, largemouth bass collected in the Delta from areas near DSM2 output locations were used to calculate the geometric mean selenium concentration in whole-body fish (Foe 2010a). The ratio of the estimated selenium concentration in fish to measured selenium in whole-body bass was used to evaluate each fish model and to focus refinements to the model. The models evaluated are presented in the following subsections.

### 4.B.4.1 Bioaccumulation in Whole-Body Fish

Seven models were evaluated for estimating whole-body selenium concentrations in fish. The basic models were refined by dietary fraction and input parameters to provide a model that would most closely represent conditions in the Delta. Each model is described in this section.

Model 1 was a basic representative of uptake by a forage fish, and Models 2 and 3 calculated sequential bioaccumulation in longer foodwebs representative of predatory fish of increasing complexity as shown below:

- Model 1: Trophic level 3 (TL-3) fish eating invertebrates

$$C_{fish} = C_{particulate} \bullet TTF_{invertebrate} \bullet TTF_{fish} \quad \textbf{[Eq. 9]}$$

- Model 2: Trophic level 4 (TL-4) fish eating TL-3 fish

$$C_{fish} = C_{particulate} \bullet TTF_{invertebrate} \bullet TTF_{fish} \bullet TTF_{fish} \quad \textbf{[Eq. 10]}$$

- Model 3: TL-4 fish eating TL-3 fish eating TL-3 and TL-2 invertebrates

$$C_{fish} = C_{particulate} \bullet TTF_{invertebrate} \bullet TTF_{invertebrate} \bullet TTF_{fish} \bullet TTF_{fish} \quad \textbf{[Eq. 11]}$$

Where:

$C_{fish}$ = concentration of selenium in fish (µg/g dw)

$C_{particulate}$ = concentration of selenium in particulate material (µg/g dw)

$TTF_{invertebrate}$ = Trophic transfer factor from particulate material to invertebrate

$TTF_{fish}$ = Trophic transfer factor from invertebrate or fish to fish

In each model, the particulate selenium concentration was estimated using Equation 2 and a default $K_d$ of 1,000. The average TTFs for invertebrates (2.8) and fish (1.1) were used in each model. The



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outputs of estimated selenium concentrations and the ratios of estimated fish selenium concentration to measured bass selenium concentration for Models 1, 2, and 3 were calculated.

Model 1 tended to underestimate the whole-body selenium concentrations in fish compared to bass data reported in Foe (2010a). This was most likely because Model 1 was estimating a forage fish (TL-3), whereas bass are a predatory fish with expected higher dietary exposure. Consequently, Model 1 was not developed further as the selenium bioaccumulation model to represent fish in the Delta.

Models 2 and 3 are both representative of predatory fish, but Model 2 was very similar to Model 1 in distribution of data and in underestimating bass data. Conversely, Model 3 had a larger distribution and greater variation in the data and significantly overestimated the bass data. These models were used as the basis for Models 4 and 5.

Models 4 and 5 were developed to represent a mixed diet using prey fractions to characterize the diet of fish in the Delta, as follows:

- Model 4: 50% of Model 2 and 50% of Model 3

$$C_{fish\ Model\ 4} = (0.5 \bullet C_{fish\ Model\ 2}) + (0.5 \bullet C_{fish\ Model\ 3}) \quad \textbf{[Eq. 12]}$$

- Model 5: 75% of Model 2 and 25% of Model 3

$$C_{fish\ Model\ 5} = (0.75 \bullet C_{fish\ Model\ 2}) + (0.25 \bullet C_{fish\ Model\ 3}) \quad \textbf{[Eq. 13]}$$

Models 4 and 5 used the default $K_d$ (1,000), average invertebrate TTF (2.8), and average fish TTF (1.1). The outputs of estimated selenium concentrations and ratios of the estimated selenium concentration in fish to measured selenium concentration in bass data for Models 4 and 5 were calculated. Data distribution and variation were comparatively large in Model 4. Model 5 was relatively predictive of bass data but was not considered representative of the general population of predatory fish in the Delta. Consequently, it was determined that Model 2 was the most representative of the prey base used by fish in the Delta (i.e., number of trophic levels in the model); therefore, further evaluation and refinement of the selenium bioaccumulation model was limited to Model 2.

In addition, review of Models 1 through 5 indicated that the default value of 1,000 for $K_d$ was not representative of the Delta's potentially high variability and uncertainty with regard to residence time. The Delta tends to have a long water-residence time and receives upstream contributions of selenium, and greater recycling and higher concentrations of selenium entering the foodweb are expected. Model 6 was developed using an extrapolated $K_d$ value of 1,400 with Model 2 (Equation 10). The average invertebrate and fish TTFs were used. Model 6 was generally predictive of bass data (ratio median 1.04). The outputs of estimated selenium concentrations and ratios of the estimated selenium concentration in fish to measured selenium concentration in bass data for Model 6 were calculated.

Model 7 was a further refinement whereby site-specific data for dissolved selenium in water and selenium in particulate samples collected in the Delta (Lucas and Stewart 2007) were used to calculate a site-specific $K_d$ of 1,760 (geometric mean). Model 7 used the more representative site-specific $K_d$ (1,760) with Model 2 (Equation 10) and the average invertebrate and fish TTFs (2.8 and 1.1, respectively). The outputs from Model 7 slightly overestimated selenium concentrations in fish compared to selenium concentrations in bass (ratio median 1.30).



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Model 8 used the site-specific $K_d$ (1,760) and the average fish TTF (1.1). The invertebrate TTF was revised so that mayflies and stoneflies were not included in the average, because these species would not be readily available in the Delta to contribute to fish or bird diets. The revised invertebrate TTF of 2.1 was used in Model 8.

As expected in a large, complex, and diverse ecological habitat such as the Delta, variations in the data distribution and in the outputs of all models including Model 8 (minimum ratio 0.45, maximum ratio 2.21, and median ratio 0.98) were observed. The variation in the models' outputs is influenced primarily by (1) the selenium concentration in water, used to estimate the selenium concentration in fish tissue, and (2) the measured selenium concentration in bass. Variation in selenium concentrations in water among the years was small, so the variation in selenium concentrations in bass was the primary factor determining the temporal variation among the models. One prominent outlier was observed in all models, seasons, and years as shown by the overestimation of selenium concentration in fish to measured selenium in bass collected at Vernalis. The overestimation is likely the result of high selenium concentrations in water calculated during different years (1999–2007) from those when bass were collected (2000, 2005, and 2007).

Data from Year 2000 were the most predictive in estimating selenium concentrations in fish tissue compared to measured selenium concentrations in bass with Model 8 (minimum ratio = 0.53, maximum ratio = 2.21, and median ratio = 0.98). Foe (2010a) reported the water-year type for 2000 as "above normal" for both the Sacramento River and San Joaquin River watersheds. It came after wet water years and was followed by dry water years. Year 2005 selenium concentrations in bass were comparatively lower than those estimated for Year 2000. Year 2005 was wetter than Year 2000 (reported as above normal for the Sacramento River watershed and wet for the San Joaquin River watershed) and occurred between periods of wetter water years than reported for Year 2000. As expected in a wet water year, the water-residence time is shorter, resulting in less selenium recycling and lower concentrations of selenium entering the foodweb. Under these influences, Model 8 tended to overestimate selenium concentrations in fish for Year 2005 (minimum ratio = 0.79, maximum ratio = 2.12, and median ratio = 1.21). For Year 2007, the model generally underestimated the comparatively higher measured selenium concentration in bass (minimum ratio = 0.45, maximum ratio = 1.57, and median ratio = 0.62). Water Year 2007 was reported as dry (Sacramento River watershed) and critically dry (San Joaquin River watershed). It came after wet water years and was followed by critically dry water years. This dry water year resulted in a longer water-residence time, greater selenium recycling, and higher concentrations of selenium entering the foodweb. Because the influences of a dry water year were not captured in the selenium concentrations in water and were reflected only in bass, Model 8 underestimated selenium concentrations in bass for Year 2007. Therefore, these results illustrate how Model 8 best predicts selenium concentration in fish during normal to wet water years but not dry water years. However, as shown above, Model 8 also can represent selenium bioaccumulation when all water-year types are combined (represented by 2000, 2005, and 2007).

Further evaluation of water-year effects on selenium concentration in bass concluded that a more representative model was needed for dry water years. Therefore, Model 9 used an extrapolated $K_d$ of 2,840, the revised invertebrate TTF of 2.1, and the average fish TTF of 1.1 with Model 2 to provide a better fit for the bass data in dry water years. The outputs of estimated selenium concentrations and ratios of the estimated selenium concentration in fish to measured selenium concentration in bass data for Model 9 were calculated.



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## *No comments*

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Model 8 is relatively predictive of selenium concentration in whole-body bass during normal to wet water years (ratio median 1.04) for all water years (ratio median 0.98) and Model 9 is considered predictive for dry water years (ratio median 1.00) These models were selected as the selenium bioaccumulative models to estimate selenium concentration in whole-body fish in the Delta and are summarized below for ease of reference.

Model 8: Trophic level 4 (TL-4) fish eating TL-3 fish

$$C_{fish} = C_{particulate} \bullet TTF_{invertebrate} \bullet TTF_{fish} \bullet TTF_{fish}$$

*Where*: **[Eq. 14]**

$$C_{particulate} = K_d \bullet C_{water}$$

- Model 9: Trophic level 4 (TL-4) fish eating TL-3 fish

$$C_{fish} = C_{particulate} \bullet TTF_{invertebrate} \bullet TTF_{fish} \bullet TTF_{fish}$$

*Where*: **[Eq. 15]**

$$C_{particulate} = K_d \bullet C_{water}$$

Where:

$C_{particulate}$ = Concentration of selenium in particulate material (µg/g dw)

$C_{water}$ = selenium concentration in water column (µg/L)

$K_d$ = equilibrium constant

$TTF_{invertebrate}$ = Trophic transfer factor from particulate material to invertebrate

$TTF_{fish}$ = Trophic transfer factor from invertebrate to fish

Because all models greatly overestimated selenium bioaccumulation in fish at Vernalis in all seasons and years, Models 8 and 9 were modified by adjusting the $K_d$ downward to reflect the lower rate of bioaccumulation at that location. The adjusted models used $K_d$ values of 850 for Model 8a and 1,130 for Model 9a. With these adjustments, Model 8a produced a ratio of 1.01 for the comparison of modeled fish to the bass data, and Model 9a produced a ratio of 1.00.

### 4.B.4.2 Bioaccumulation in Bird Eggs

The $K_d$, invertebrate TTF, and fish TTFs developed for use in fish bioaccumulation Models 8 and 9 also were used to estimate selenium uptake into bird eggs using the following two bird egg models:

- Bird Egg: Uptake from invertebrates

$$C_{bird\ egg} = C_{particulate} \bullet TTF_{invertebrate} \bullet TTF_{bird\ egg}$$

*Where*: **[Eq. 16]**

$$C_{particulate} = K_d \bullet C_{water}$$

- Bird Egg: Uptake from fish

$$C_{bird\ egg} = C_{particulate} \bullet TTF_{invertebrate} \bullet TTF_{fish} \bullet TTF_{bird\ egg}$$

*Where*: **[Eq. 17]**

$$C_{particulate} = K_d \bullet C_{water}$$



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## *No comments*

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Where:

$C_{bird\ egg}$ = concentration of selenium in bird egg (µg/g dw)

$C_{particulate}$ = concentration of selenium in particulate material (µg/g dw)

$C_{water}$ = selenium concentration in water column (µg/L)

$K_d$ = equilibrium constant

$TTF_{invertebrate}$ = trophic transfer factor from particulate material to invertebrate

$TTF_{fish}$ = trophic transfer factor from invertebrate to fish

$TTF_{bird\ egg}$ = trophic transfer factor from invertebrate or fish (depending on diet) to bird egg

For normal to wet years, the site-specific $K_d$ value (1,760), revised invertebrate TTF (2.1), average fish TTF (1.1), and mallard bird egg TTF (1.8) were used. For dry years, the revised $K_d$ (2,840), revised invertebrate TTF (2.1), average fish TTF (1.1), and mallard bird egg TTF (1.8) were used..

## 4.B.5 Bioaccumulation in Fish Fillets

Selenium concentrations in whole-body fish were converted to selenium concentrations in skinless fish fillets. The regression equation provided by Saiki and coauthors (1991) for largemouth bass from the San Joaquin River system was considered to be the most representative of fish in the Delta and was used for the conversion of these selenium concentrations as follows:

$$SF = -0.388 + 1.322\,WB \quad \textbf{[Eq. 18]}$$

Where:

$SF$ = selenium concentration in skinless fish fillet (µg/g dw)

$WB$ = selenium concentration in whole-body fish (µg/g dw)

Fish fillet data will be compared to the advisory tissue level (2.5 µg/g) in wet weight (Office of Environmental Health Hazard Assessment 2008); therefore, wet-weight concentrations were estimated from dry-weight concentrations using the equation provided by Saiki and coauthors (1991) as follows:

$$WW = DW \bullet (100 - Moist)/100 \quad \textbf{[Eq. 19]}$$

Where:

$WW$ = selenium concentration in wet weight (µg/g ww)

$DW$ = selenium concentration in dry weight (µg/g dw)

$Moist$ = mean moisture content of the species

Because moisture content in fish varies among species, sample handling, and locations, the mean moisture content of 70% as used by Foe (2010b) was used as an assumed approximation for fish in the Delta. The final equation used to estimate selenium concentration in skinless fish fillets (wet weight) from selenium concentration in whole-body fish (dry weight) is as follows:

$$SF = (-0.388 + 1.322\,WB) \bullet 0.3 \quad \textbf{[Eq. 20]}$$



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***No comments***

- n/a -

Where:

*SF* = selenium concentrations in skinless fish fillet (µg/g ww)

*WB* = selenium concentration in whole-body fish (µg/g dw)

## 4.B.6 References

### 4.B.6.1 Printed References

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### 4.B.6.2 Personal Communications

Foe, Chris. Staff Environmental Scientist. California Regional Water Quality Control Board, Central Valley Region, Rancho Cordova, CA. April 23, 2010—e-mail to Harry Ohlendorf, Technology Fellow, CH2M HILL, Sacramento, CA.

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***No comments***

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