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Kevin Buchan
Senior Coordinator, Bay Area and State Water Issues

VIA ELECTRONIC MAIL

October 5, 2012

Bruce Wolfe
Executive Officer
San Francisco Regional Water Quality Control Board
1515 Clay Street, 14th Floor
Oakland, CA 94612

Subject: North San Francisco Bay Selenium Characterization Study - Final Report

Mr. Wolfe,
The Western States Petroleum Association (WSPA) submits the Final Report for the Selenium Characterization Study (Study) on behalf of the five Bay Area refineries (Chevron, Phillips 66, Shell, Tesoro, and Valero) in accordance with Table 4 of Order R2-2010-0057, Table 13 of Order R2-2009-0079, and the Board approvals for schedule amendments.

This Report fulfills the requirements of the above mentioned orders and is consistent with our revised Study Plan approved by the Board.

Due to the size of the Report appendices (10 Mb), WSPA has uploaded the Report with appendices to the Board's FTP site (ftp://swrcb2a.waterboards.ca.gov), and we have notified your staff of this action.

WSPA and the five Bay Area refineries have greatly appreciated the collaborative efforts by Board staff in directing this Study to completion. We look forward to further engaging the Board on next steps to finalizing the Selenium TMDL.

Sincerely,

Kevin Buchan

Enclosure: Final Report (w/o appendices)

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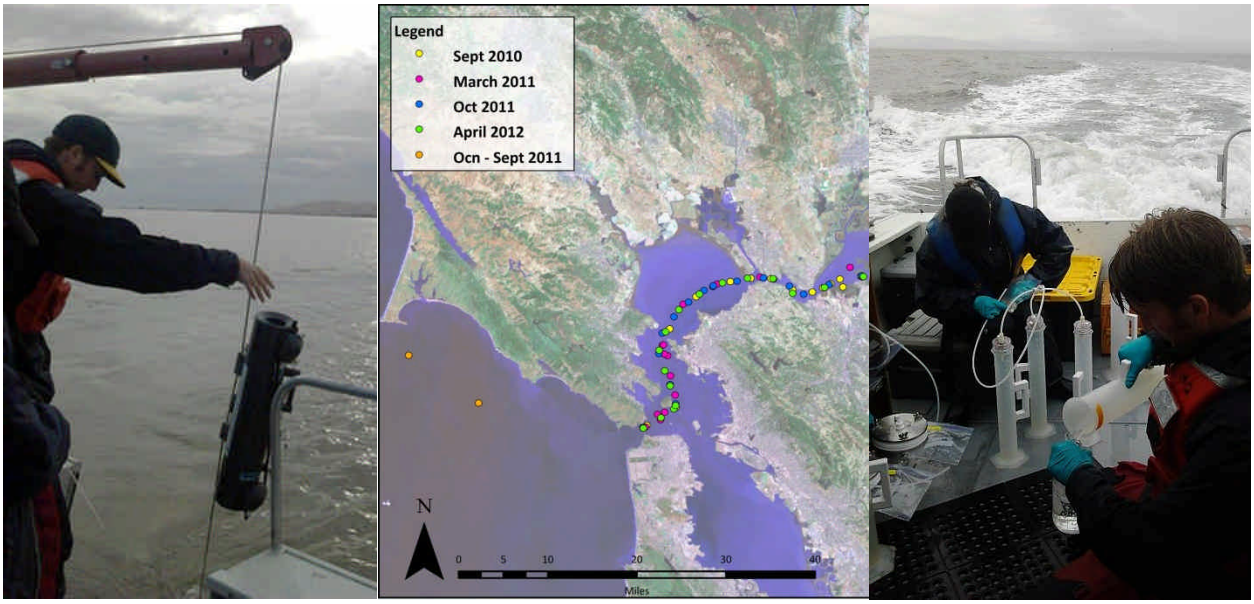
North San Francisco Bay Selenium Characterization Study

Final Report



October 5, 2012

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Executive Summary

This document describes the sampling design, field sampling activities and the analytical results of the North San Francisco Bay Selenium Characterization Study. This study was conducted in response to the Regional Water Quality Control Board's permit requirement and 2010 Amendment of Waste Discharge Requirements for San Francisco Bay Region Refineries that was adopted in March 2010. The amendment directed the five refineries in North San Francisco Bay to implement effluent and receiving water selenium characterization studies. The overall goal of the Selenium Characterization Study was to obtain information on current conditions of selenium (Se) distribution and speciation under representative hydrologic conditions.

There were three main sampling elements associated with the study plan: (1) Transect sampling along a salinity gradient in the estuary, including locations in the Sacramento and San Joaquin Rivers, (2) Receiving-water sampling near the refinery effluent outfalls of each of the five refineries to characterize near-field Se concentrations and speciation; and, (3) Refinery effluent sampling at locations equivalent to the existing effluent compliance point.

The transect and receiving-water sampling events were successfully conducted in September 2010, March and October 2011 and April 2012. Monthly sampling of refinery effluents was performed from September 2010 to August 2011. The focus of the data-collection and sample-analysis efforts was on the measurement of selenium concentrations in the water column and suspended particles, and the determination of selenium speciation and particulate selenium content in the estuary, refinery receiving water and refinery effluent (Table ES-1).

In addition to the sampling described in Table ES-1, samples were also collected at tributaries that flow directly into North San Francisco Bay, as distinct from the larger tributaries (such as San Joaquin and Sacramento Rivers) that flow to the bay through the Delta.

A numerical model of selenium fate and transport in the North San Francisco Bay was developed in support of the development of a selenium TMDL in this water body (Tetra Tech, 2010; Chin et al, 2012). One of the objectives of the Selenium Characterization Study was to verify that the values for the dissolved and particulate Se concentrations used in the model calibration were appropriate. As part of this study, the model was run with the new updated flow and selenium load inputs derived from the 2010 – 2012 sampling and analysis results.

Table ES-1
Analytical Parameters by Sample Element

Parameter	Sample Element		
	Effluent	Transect	Receiving Water (Near Outfalls)
Dissolved			
Salinity		●	●
Phosphate		●	
Nitrate+Nitrite		●	
Silicate		●	
Se(IV)	●	●	●
Se (VI)	●	●	●
Se (Total)	●	●	●
Se (Organic)	●	●	●
Particulate			
Chlorophyll-a		●	
Phaeophytin-a		●	
Se(Total)	●	●	●
Se(IV+VI)	●	●	●
Se(0)	●	●	●
Se(Organic)	●	●	●
Total Suspended Matter (TSM)	●	●	●

Transect and Tributary Sampling

In two dry- and two wet-weather transects, samples were collected from an average of 22 sites between the Golden Gate Bridge and the Sacramento River at Rio Vista, CA along salinity increments of approximately 1.5–2 parts-per-thousand (g/l); providing a range of salinities from oceanic (24–33 g/l) to riverine (<1 g/l). Samples were also collected at Freeport on the Sacramento River and Vernalis on the San Joaquin River to measure riverine inputs. One set of samples was collected in the nearshore zone, north of the Golden Gate Bridge.

A composite of the 2010–2012 transect station locations is shown in Figure ES-1 and of the 2012 tributary locations in Figure ES-2.

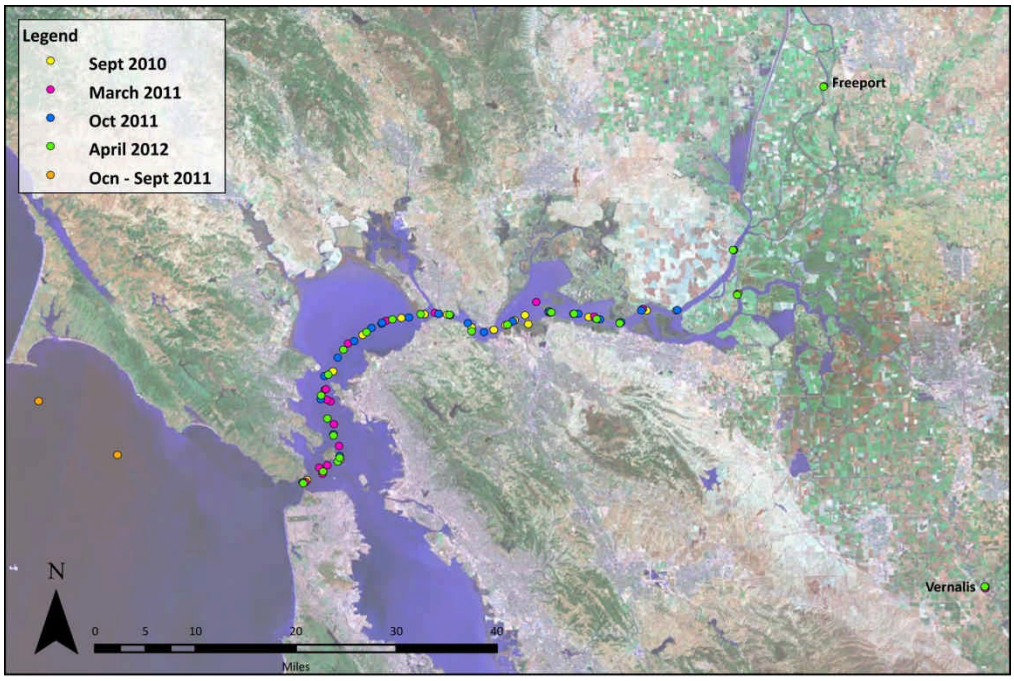

Figure ES-1
Transect sample locations (2010–2012).

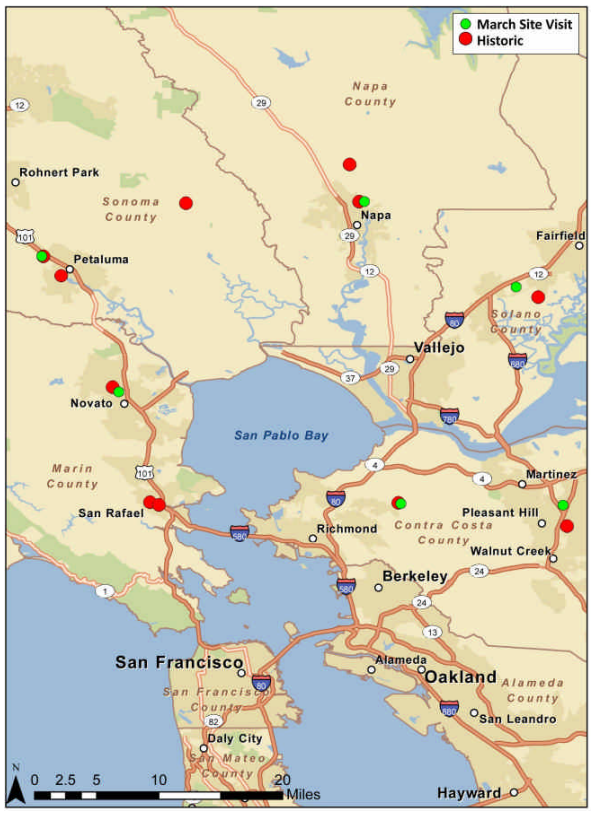

Figure ES-2
Tributary locations sampled on March 14–15, 2012 (green symbols), and historic sampling conducted in previous efforts (red symbols).

The sampling design, along with the existence of equivalent historical data, provide the ability to make comparisons of selenium concentrations under similar sampling conditions (e.g., dry-season conditions) between sampling dates. For example, the particulate Se concentration measurements from dry-weather transects in 1999, 2010 and 2011 are presented in Figure ES-3. Differences in the measured concentrations (expressed in µg/g) and in the variability within the individual transects (e.g., the 1999 and 2011 transects) are evident among the three sampling events. Figure ES-3 also shows the higher concentrations of particulate Se at the riverine boundary locations (Freeport and Vernalis) and at the offshore sampling locations. These boundary conditions were identified as a data gap in prior work and have not been directly measured in any previous effort.

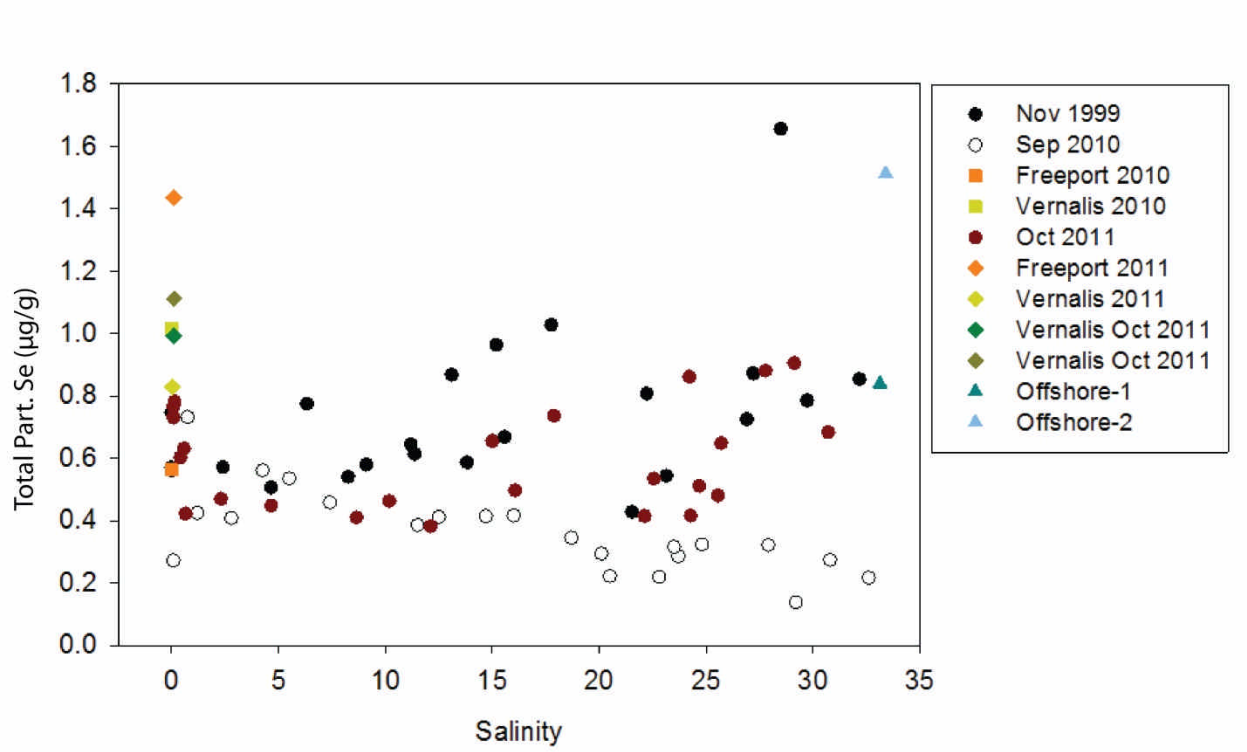

Figure ES-3
Dry weather total particulate selenium concentrations across the estuary with data from November 1999, September 2010 and October 2011. Also shown are concentrations sampled in the riverine sources at Freeport (Sacramento River) and Vernalis (San Joaquin River) as well as from two offshore locations.

Overall the transect sampling showed that total dissolved selenium concentrations in the estuary were similar across the four sampling events in 2010 - 2012. Total particulate selenium concentrations were about an order of magnitude lower than dissolved phase concentrations (when both quantities are expressed as µg/l). Both dissolved and particulate selenium concentrations were elevated at Vernalis on the San Joaquin River. Greater variability in selenium species (selenite, selenite, selenide, and elemental selenium) was observed in the dissolved and particulate phases. Kd values (ratio between dissolved and particulate concentrations) were computed for this effort for all samples, and indicate large variability by location and season. The tributary data obtained in this effort (Appendix F) update previous data from multiple studies. These data confirm the significance of the tributary loads that were previously estimated, and also provide speciation information that was not previously reported. These data show that tributary particulate selenium loads are larger than the refinery particulate loads.

Receiving-Water Sampling

Sampling near the refinery outfalls was challenging because of the need to locate the samples within a few meters of the diffusers, but these new data provide a detailed characterization of selenium concentrations near the discharge locations. The results showed higher concentrations for dissolved selenium compared to the corresponding mid-estuary stations, for both dry weather and wet weather events. However, this was not the case for particulate selenium concentrations, which were similar to the estuary concentrations.

Refinery Effluent

Dissolved and particulate selenium by species were sampled directly from the five refinery effluents on a monthly basis. Refinery effluent selenium was mostly in the dissolved form, with a small fraction of particulate selenium. Dissolved selenium concentrations in the effluents were generally in the form of selenate. Selenate concentrations in the refinery effluents generally range between 2–18 µg/L, with concentrations varying among refineries and over time. Generally median selenate concentrations were below 10 µg/L for most of the time periods sampled.

Total particulate selenium concentrations in the refinery effluents ranged from 0.03-0.6 µg/L. When expressed as µg/g, total particulate selenium concentrations generally ranged from 10-190 µg/g. Speciation of particulate selenium in refinery effluents was dominated by elemental selenium, followed by particulate organic selenide and particulate selenite and selenate. TSM concentrations generally ranged between 2–20 mg/L in the effluents sampled.

Modeling

The modeling approach used is one-dimensional, where the estuary is represented as a series of 33, 3-km wide cells from Rio Vista in the Sacramento River/Delta to the Golden Gate, and was developed using a tool called ECoS (Tetra Tech, 2010). The modeling approach is suited for the simulation of large-scale processes. Small-scale features of the data, such as the concentrations near the refinery discharge cannot be represented through this model.

The modeling presented in this work focused on mid-estuary data on the different selenium species. The model was able to represent the observations of both dissolved and particulate selenium across six different events spanning a decade (4 current, and two from 1999) and different loading and hydrologic conditions. This was done using updated model inputs, but largely unmodified selenium transformation rates. The sole change in uptake rates related to the phytoplankton uptake of selenium. However, due to simplifications in the model, small-scale variations in particulate selenium are not always captured. These may be caused by local variations in phytoplankton growth and resuspension of sediments that are not represented in the model.

Linkage to Permit Elements

The primary goal of the Selenium Characterization Study was to obtain information on current conditions of selenium (Se) distribution and speciation under representative hydrologic conditions. The use of these new data was identified in the six study elements presented in the Selenium Characterization Study Plan and discussed below:

1. **Sampling results, data interpretation, and conclusions, such as receiving water and mixing zone characterization, seasonal variability, etc**. In addition to the analyses and interpretations of the data presented in this report, the complete data set is presented in the

report appendices. These data can be used to conduct additional modeling runs and to explore new hypotheses associated with the development of the North San Francisco Bay Selenium TMDL.

2. **Effluent Characterization**. The monthly effluent samples and the receiving-water samples provide new and important information that have been used to characterize the dissolved and particulate speciation of the discharged selenium from refineries.

3. **Determination if there is reasonable potential for selenium in the discharge to violate the Basin Plan's narrative bioaccumulation objective through the use of pertinent models.** Data on receiving water concentrations, obtained in proximity to the discharge locations are described and compared with concentrations observed at mid-estuary locations. In addition, the new modeling work presented in this report supplements the previous modeling efforts conducted as part of the development of the Selenium TMDL. The existing model provides the basis for the evaluation of a range of applicable bioaccumulation standards.

4. **Comparison of near-field selenium water column concentrations to applicable numeric objectives.** The current water column objective of 5 µg/l is not exceeded in the near field concentrations sampled over four sampling events. Fish and wildlife criterion development is underway for the San Francisco Bay-Delta Estuary that could result in a new water column objective. The model developed as part of the TMDL effort and further advanced with this study provides the ability to assess the practicability of alternative numeric objectives.

5. **Demonstration of spatial and temporal extent to which the objectives and other relevant guidelines, are being exceeded.** Total selenium data are presented over the transect across different seasons for direct evaluation against specific numeric objectives. All concentrations in the Bay are below the 5 µg/l water quality criterion.

6. **Determination whether selenium levels impact foodweb and wildlife and/or contribute to bioaccumulation**. The ECoS model application as previously developed and calibrated (Tetra Tech, 2010) was evaluated for the new conditions, utilizing the most current information on inflows and selenium loads from point and non-point sources. The modeling was updated to compute through 2012, among other elements, the particulate selenium concentrations, the pathway through which selenium uptake in benthic feeding organisms occurs. This updated modeling with the new data is a more robust tool for evaluating the bioaccumulation in the bay, and the linkage between sources and biota concentrations. Previously published work described selenium bioaccumulation in clams, fish, and birds (Chen et al., 2012); however no new data on these compartments have since been reported to assess conditions in 2011 and 2012.

1 Introduction

The Regional Water Board's 2010 Amendment of Waste Discharge Requirements for San Francisco Bay Region Refineries, Order R2-2010-0057, was adopted in March 2010. It directed the five refineries in North San Francisco Bay to implement effluent and receiving water selenium characterization studies as set forth in Table 4 of the Order (RWQCB, 2010). The goal of this effort was to obtain information on current conditions of selenium (Se) distribution and speciation under representative hydrologic conditions.

The *North San Francisco Bay Selenium Characterization Study Plan (2010–2012)* prepared by the Western States Petroleum Association (WSPA, 2010) provided a description of the number and location of samples, the laboratory analytical methods, and the reporting requirements associated with the characterization study. The Study Plan described four sampling transect and refinery receiving water events over the two-year sampling program. The sampling events were successfully conducted in September 2010, March and October 2011 and April 2012. In addition to the transect and refinery receiving water sampling, monthly sampling of refinery effluents was performed from September 2010 to August 2011 and six tributaries to the North San Francisco Bay were sampled in March 2012. The results from all of these efforts are summarized in this report.

The Study Plan provided a general description of the sampling design and the prescribed sampling locations. In this report, detailed descriptions of the sampling locations and methods are presented in Section 2. A graphical representation of the combined transect and refinery receiving water sampling locations for all four events is presented as well as a graphic showing the locations of the tributary samples. A description of the factors that affected the selection of these locations is also included. Specific sampling coordinates and locations for each of the four sampling events are presented in Appendix A.

In Section 3, the laboratory analytical methods, including minor modifications to these methods that have been implemented, are described.

Data and interpretation are provided in Sections 4 and 5. The results of the laboratory analyses are presented in Section 4 and the modeling evaluation is presented in Section 5. The goal of this final report is to address the elements that were outlined in the characterization study schedule and in the study plan. These elements (in **bold**) and related report contents are described below:

a) **Sampling results, data interpretation, and conclusions, such as receiving water and mixing zone characterization, seasonal variability, etc.** All sampling data are presented in graphical and tabular form in the main report and supporting Appendix B, and provided in electronic format. These new data are directly comparable to measurements of the concentration, chemical form (speciation) and distribution of Se previously made during 1999–2000 (Cutter and Cutter, 2004 and Doblin et al., 2006).

b) **Effluent characterization.** The monthly effluent samples and the receiving-water samples provide new data on the dissolved and particulate concentrations of the discharged selenium from refineries. These data were used to update the load contribution of the refineries to the total dissolved and particulate loads to the Bay. The

total selenium data previously available was updated with new data on selenium speciation in the discharge.

c) **Determination if there is reasonable potential for selenium in the discharge to violate the Basin Plan's narrative bioaccumulation objective through the use of pertinent models.** Data on receiving water concentrations, obtained in proximity to the discharge locations are described and compared with concentrations observed at mid-estuary locations.

d) **Comparison of near-field selenium water column concentrations to applicable numeric objectives.** The receiving water sampling results provide the ability to make direct comparisons to existing water quality objectives.

e) **Demonstration of spatial and temporal extent to which the objectives and other relevant guidelines, are being exceeded.** Total selenium data are presented over the transect across different seasons for direct evaluation against specific numeric objectives.

f) **Determination whether selenium levels impact foodweb and wildlife and/or contribute to bioaccumulation.** A biogeochemical model of selenium in the bay, relating dissolved and particulate selenium, is presented and updated using the current data. Particulate selenium is the pathway through which selenium is thought to enter the food web. This model may be used to evaluate selenium impacts on the San Francisco Bay food web under current and future conditions.

Overall, this report provides considerable new information on the distribution and behavior of selenium in San Francisco Bay and represents a major update after a gap of nearly a decade. This report integrates the data with modeling previously done, and can be used to develop scenarios for improving management of selenium in the San Francisco Bay region.

2 Study Plan Description and Field Activities

The Study Plan (WSPA, 2010) contains seven elements ("a" through "g"). Elements a and b describe the three types of samples that are required to be collected and analyzed: (1) Transect samples collected along a salinity gradient in the estuary, including locations in the Sacramento and San Joaquin Rivers, (2) Refinery receiving-water samples collected near the effluent outfalls of each of the five refineries to characterize near-field Se concentrations and speciation; and, (3) Effluent samples collected at a location equivalent to the existing effluent compliance point. Element c describes the four sampling events over the 2010–2012 study period. Element d provides guidance for the selection of sampling protocols and analytical methods. Element e identifies the chemical parameters that are required to be measured. Element f provides guidance for the data analysis and interpretation methods, and Element g provides the schedule for the sampling and completion of the characterization study. Elements a–c are presented in Table 2-1.

Table 2-2 lists the chemical parameters, specified in Element e of the Study Plan, that were measured for each sample type. Section 4 of this report includes a presentation and discussion of all data available to date.

Table 2-1
Sample Plan Description

Element	Permit Language	Plan
a	Effluent and receiving water sampling locations (the effluent sampling location may be the existing effluent compliance sampling point; receiving water sampling locations shall be within a 100-foot radius of the outfall to characterize near-field concentrations and speciation);	Monthly effluent samples and receiving water transects at the 5 refineries during the first year sampling.
b	Receiving water sampling along transects from the Pacific Ocean (Golden Gate) to the Sacramento River (Rio Vista) and San Joaquin River (USGS Station 757), including sampling in the freshwater portions of the rivers at Vernalis (San Joaquin River) and Freeport (Sacramento River);	Transect sampling in the estuary, stations in the Sacramento and San Joaquin Rivers (at Vernalis and Freeport), and an "oceanic" site near the Golden Gate Bridge
c	Sampling and analysis protocols (including means to evaluate seasonal conditions under low and high flows from the Sacramento / San Joaquin River Delta, selenium concentrations in the water column and suspended particles, and speciation and particulate selenium content in the effluent);	One dry season sampling in 2010, one wet and one dry season sampling in 2011, and one wet season sampling in 2012

Table 2-2
Analytical Parameters by Sample Type

Parameter	Sample Type		
	Effluent	Transect	Receiving Water (Near Outfalls)
Dissolved			
Salinity		•	•
Phosphate		•	
Nitrate+Nitrite		•	
Silicate		•	
Se(IV)	•	•	•
Se (VI)	•	•	•
Se (Total)	•	•	•
Se (Organic)	•	•	•
Particulate			
Chlorophyll-a		•	
Phaeophytin-a		•	
Se(Total)	•	•	•
Se(IV+VI)	•	•	•
Se(0)	•	•	•
Se(Organic)	•	•	•
Total Suspended Matter (TSM)	•	•	•

2.1 2010–2012 Dry and Wet Weather Field Activities

The dry and wet weather field sampling of transect and receiving water stations occurred on the following dates:

- Dry Weather 2010: September 8–13, 2010
- Wet Weather 2011: March 14–22, 2011
- Dry Weather 2011: October 3–11, 2011
- Wet Weather 2012: April 10–16; April 25, 2012

Refinery effluent monitoring took place on a monthly basis, from September, 2010 to August, 2011. Each of these sampling activities is described below.

Transect – Dry and wet weather transect samples were collected from an average of 22 sites between the Golden Gate Bridge and the Sacramento River at Rio Vista, CA along salinity increments of approximately 1.5–2 parts-per-thousand (g/l); providing a range of salinities from oceanic (24–33 g/l) to riverine (<1 g/l). All samples were collected during a flood-tide, with the exception of the 2011 Wet Weather event samples which were collected during an ebb tide due to the timing of the tides and the necessity to collect during daylight hours. Additionally, two samples were collected in September, 2011 from an offshore location just north of the entrance to the San Francisco Bay.

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

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

Refinery Effluent – Monthly refinery effluent samples were collected by refinery staff from their discharge location and processed by Tetra Tech and Pacific EcoRisk staff. The objective of these samples was to characterize each refinery's effluent prior to discharge.

All estuary and refinery receiving-water locations were accessed by vessels operated by Pacific EcoRisk. All samples were collected by Tetra Tech staff. The offshore samples were collected and processed by Dr. Greg Bruland while aboard the RV Point Sur.

2.2 Dry and Wet Weather Sample Locations

Transect – A composite of the 2010–2012 Transect station locations is provided in Figure 2-1. Individual transect station coordinates and locations for each of the four sampling events are provided in Appendix A (Tables A-1, A-3, A-5 and A-7 and Figures A-1, A-7, A-13 and A-19).

Refinery Receiving Water – Individual refinery receiving water station coordinates for each of the four sampling events are provided in Appendix A (Tables A-2, A-4, A-6 and A-8). Receiving water stations are portrayed in Figures 2-2 through 2-8. Samples were collected at the end of the discharge pipe and 10m up-current and 10m down-current.

As discussed in greater detail in Section 4.3 of this report and portrayed in Figures 2-2 and 2-4, there were logistical and physical challenges that occurred during the September 2010 even at the Valero and Tesoro refinery outfall sites that resulted in samples not being collected according to the study plan. However, these challenges were resolved and subsequent sample collection locations were according to the study plan.

Refinery Effluent – Refinery effluent samples were collected monthly between September 2010 and August 2011 from each refinery's compliance discharge collection point.

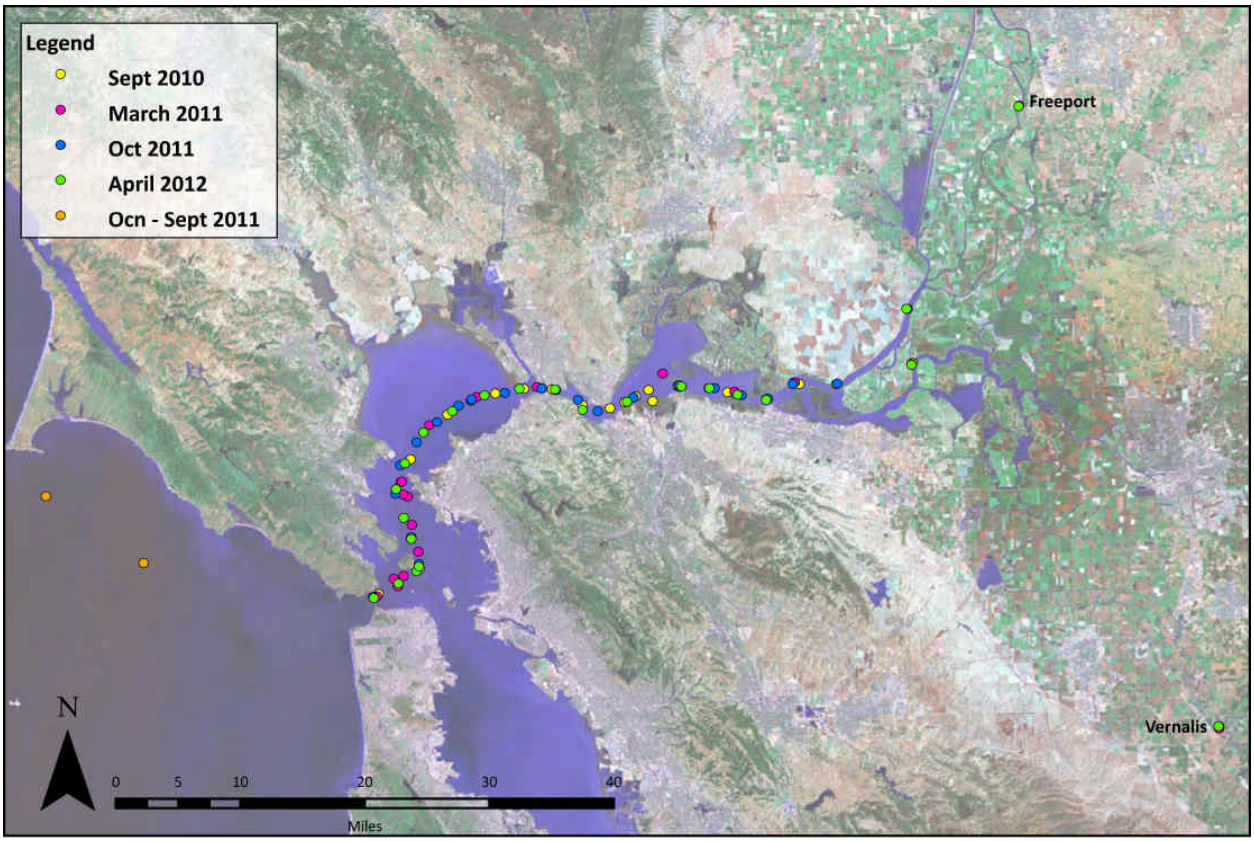

Figure 2-1
Transect sample locations (2010–2012). Offshore coastal samples were collected in September 2011.

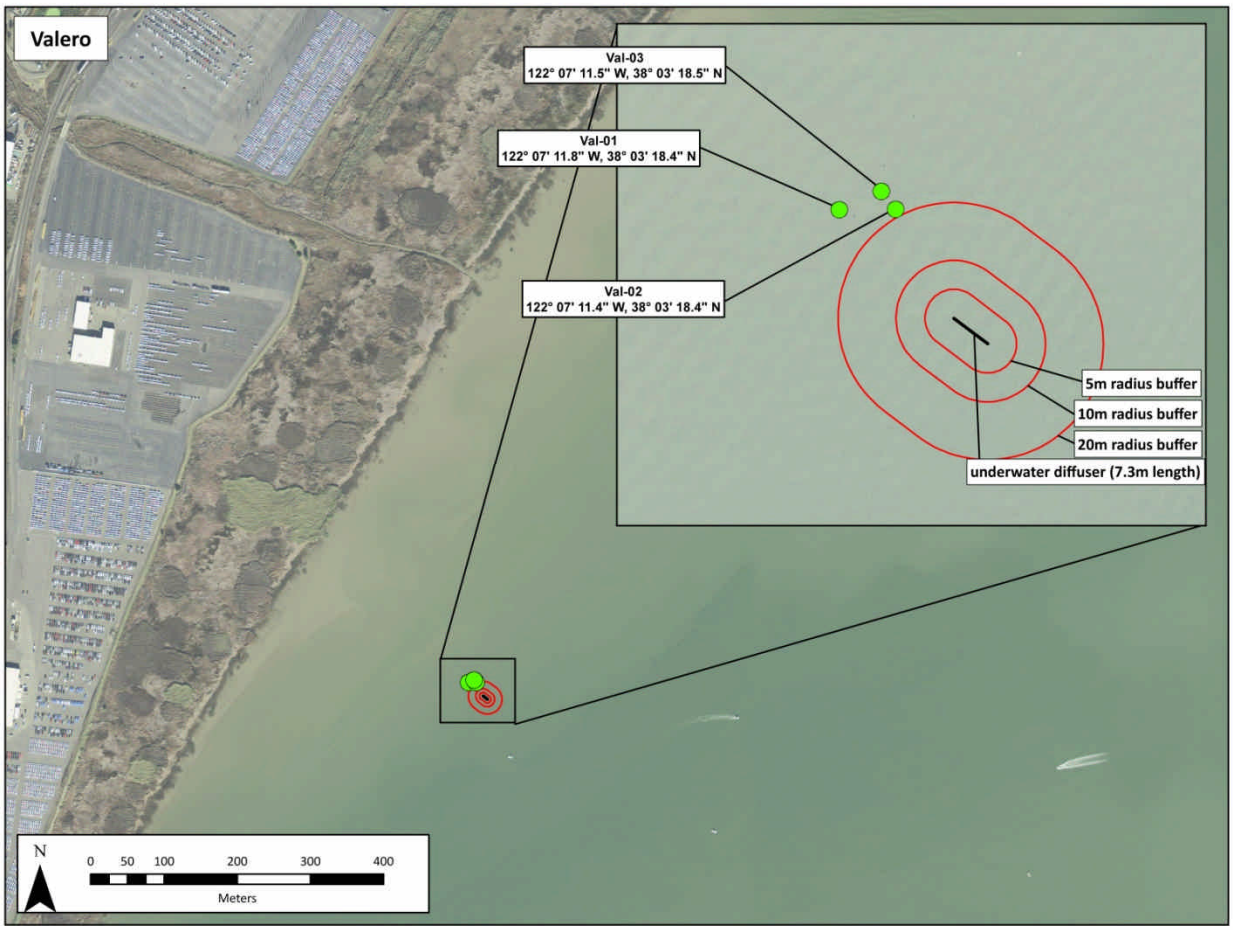

Figure 2-2
Receiving water sample locations at the Valero Refinery during the September 2010 dry weather event. Note that sample locations were outside the 20m buffer rather than at the 10m buffer as originally planned due to logistical challenges during this sampling event.

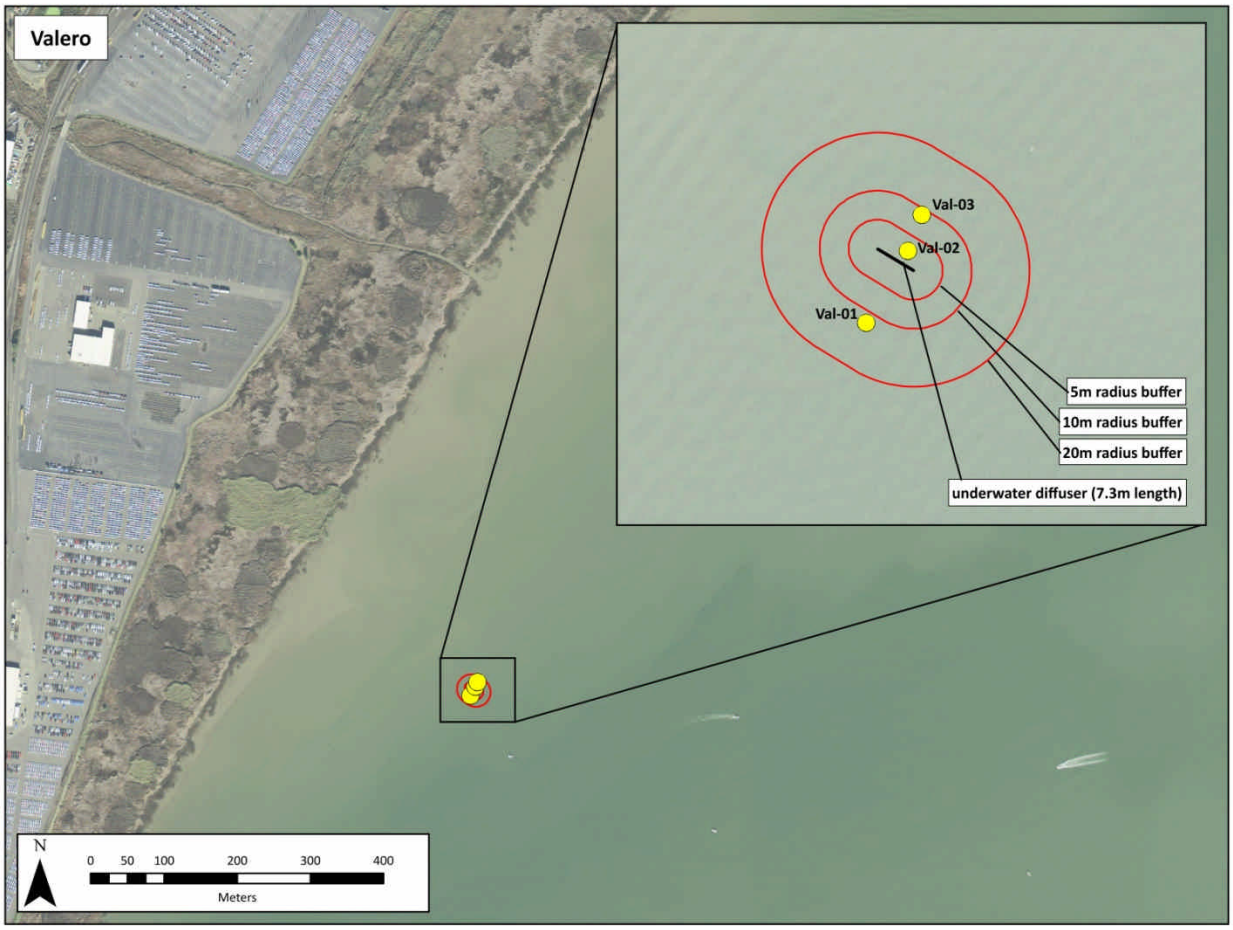

Figure 2-3
Refinery receiving water sample locations at the Valero Refinery for the 2011 and 2012 sample events.

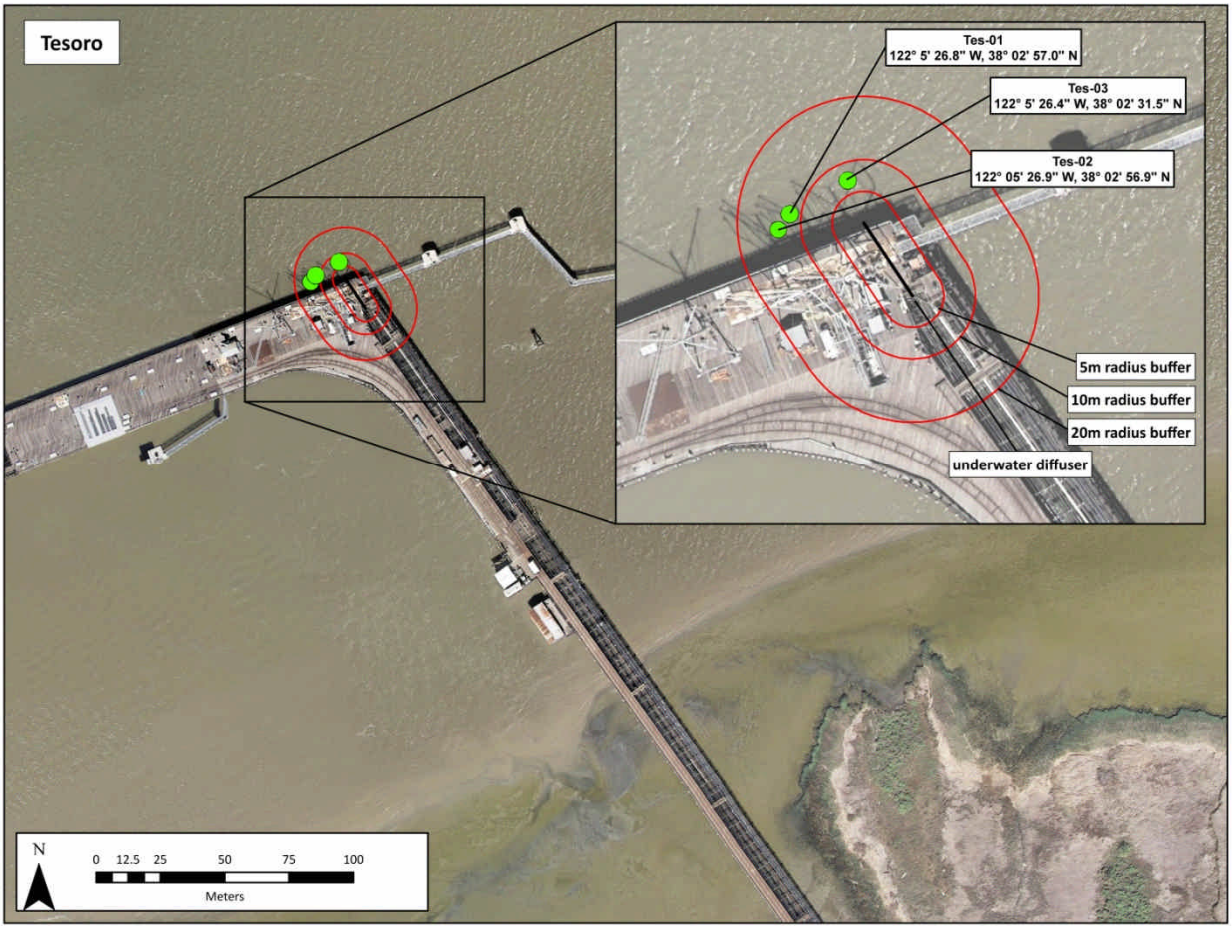

Figure 2-4
Receiving water sample locations at the Tesoro Refinery during the September 2010 dry weather event. Note that the sample locations are shifted eastward due to strong winds and currents at the time of sampling which made it impossible to collect from 10m up and down current of the diffuser.

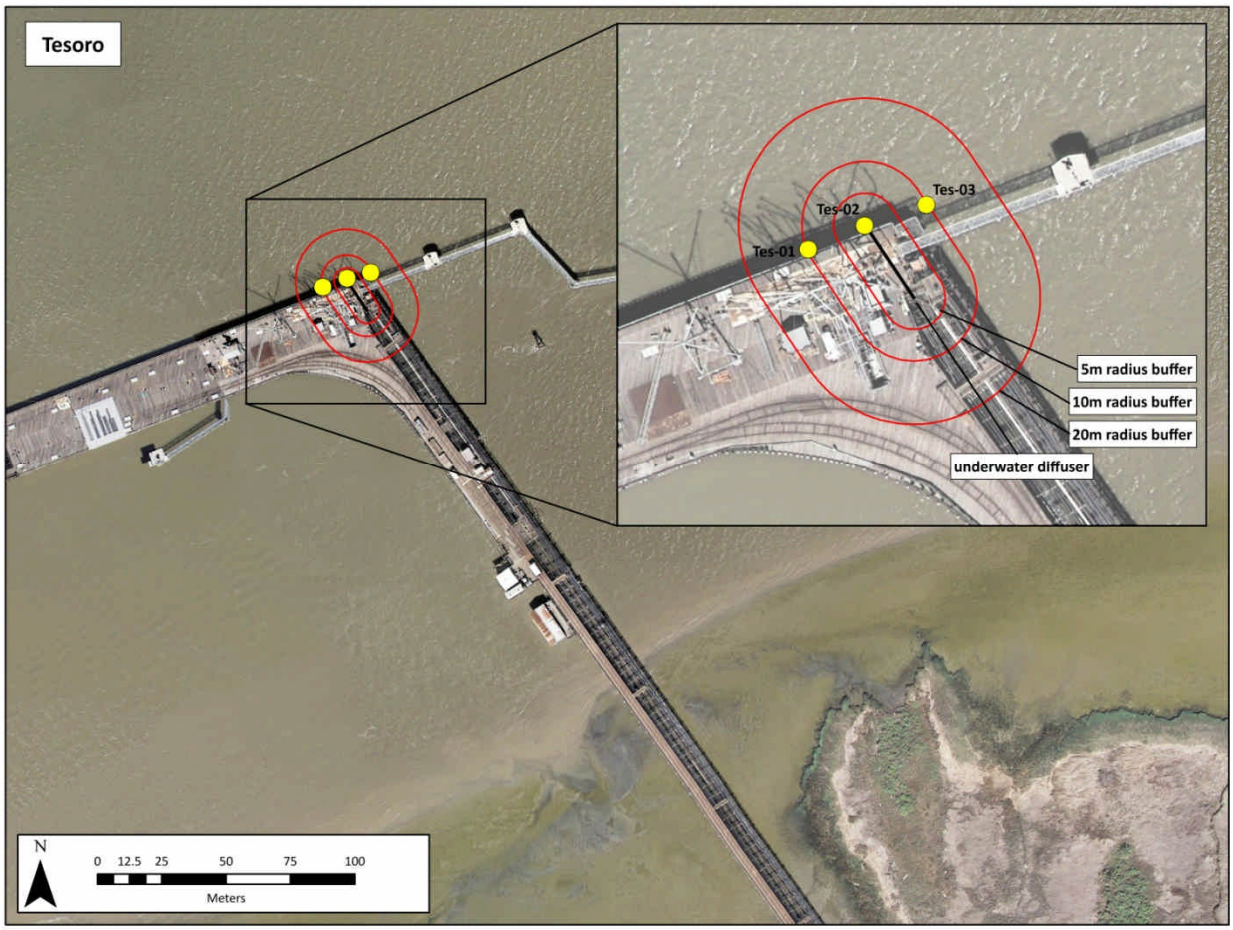

Figure 2-5
Refinery receiving water sample locations at the Tesoro Refinery for the 2011 and 2012 sample events.

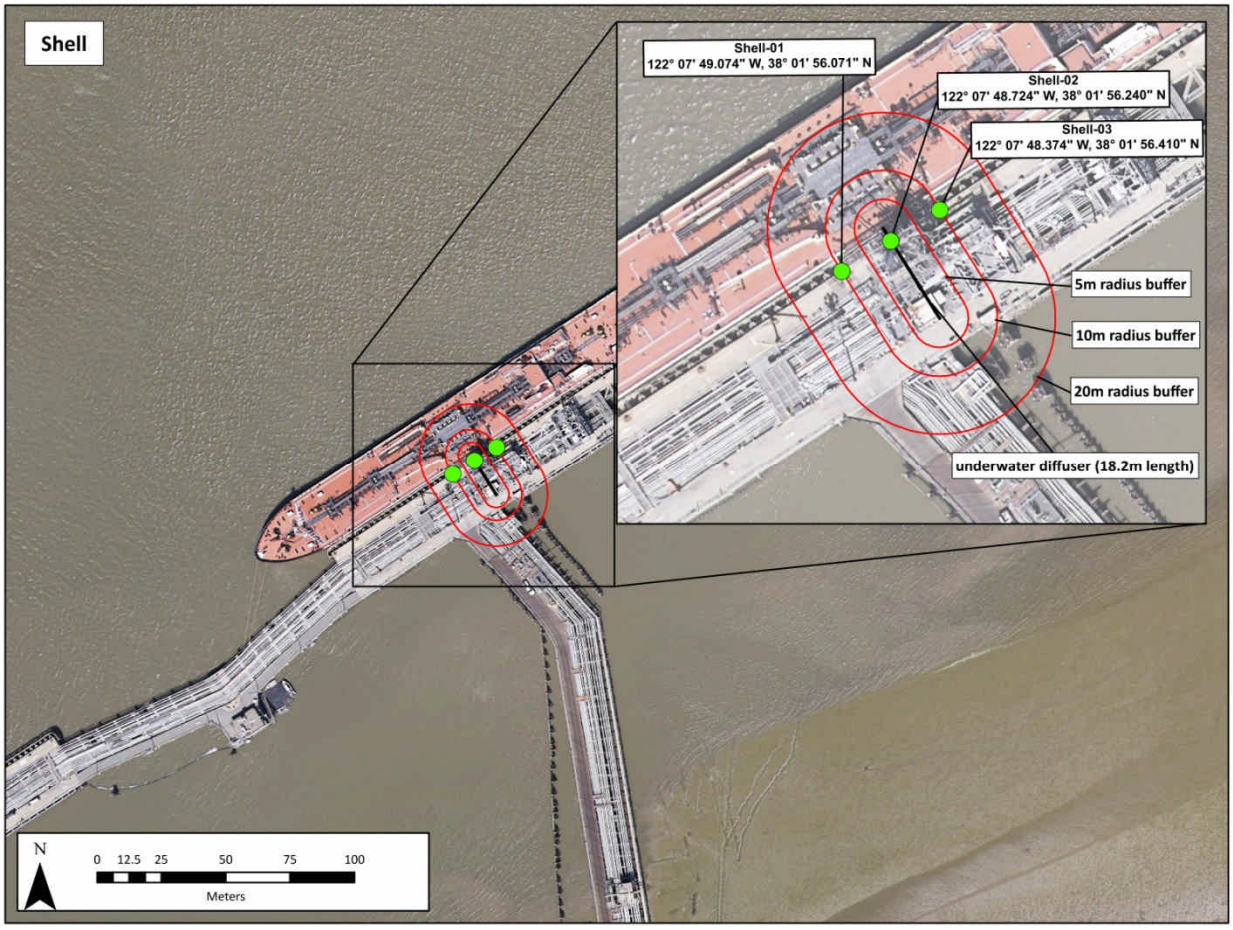

Figure 2-6
Receiving water sample locations at the Shell Refinery for the 2010, 2011 and 2012 sample events.

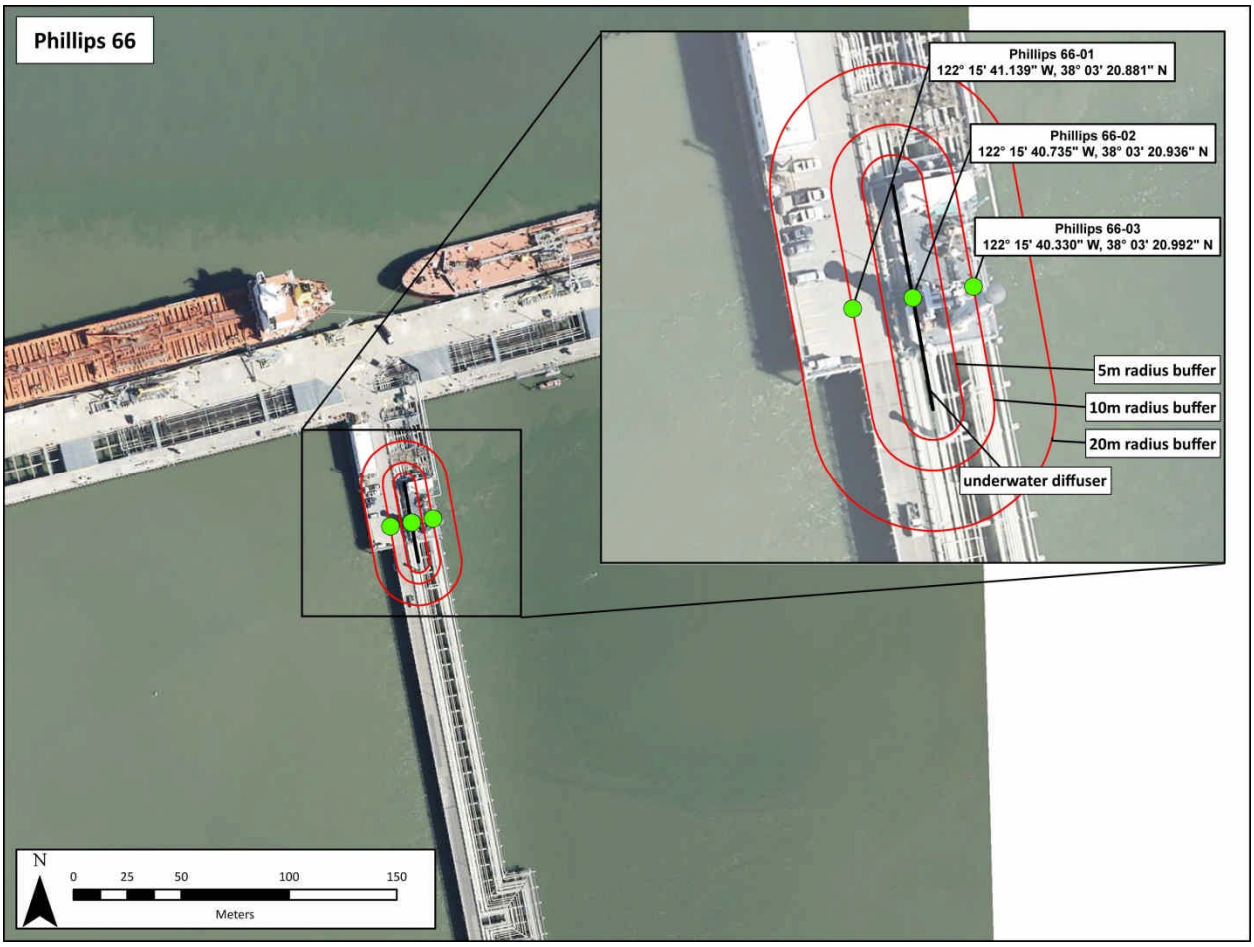

Figure 2-7
Receiving water sample locations at the Phillips 66 Refinery for the 2010, 2011 and 2012 sample events.

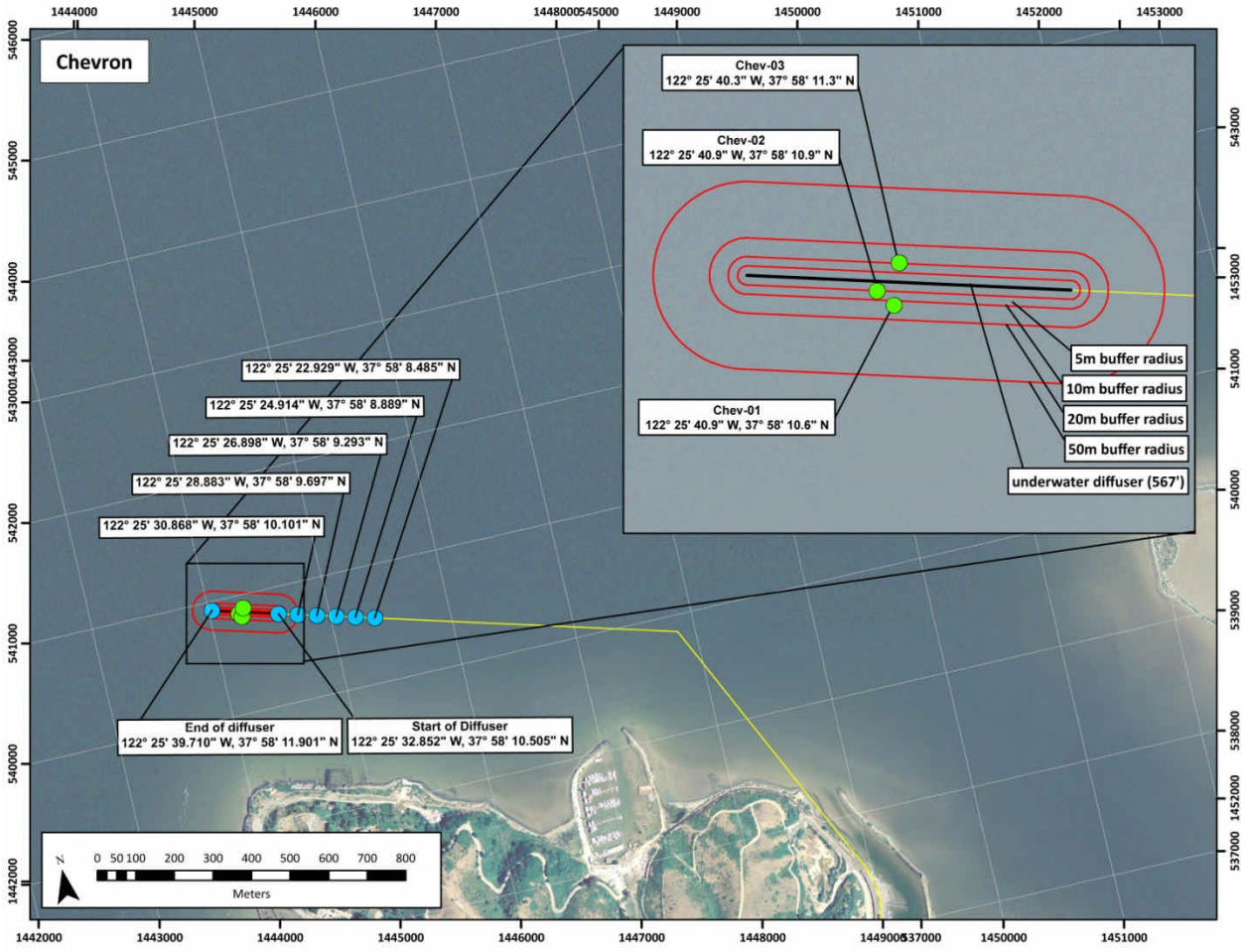

Figure 2-8
Receiving water sample locations at the Chevron Refinery for the 2010, 2011 and 2012 sample events.

2.3 Sample Collection, Processing and Shipping

Transect Samples

All transect and receiving water samples, except where noted, were collected from Pacific EcoRisk's 30' aluminum hulled research vessel outfitted with an over-side winch and onboard GPS. In addition, Dr. Ken Bruland collected two off-shore samples on September 01, 2011 from just north of the entrance to San Francisco Bay (Figure 2-1). These two samples were collected and processed onboard the RV Point Sur.

Salinity was used to determine the stations selected for the transect component of the study, with an average of 22 stations being selected along a transect from a site near the Golden Gate Bridge to the Sacramento River at Rio Vista at approximately 1.5–2.0 g/l salinity intervals. Because of the effect of tidal and river flow on the salinity gradient, the stations could not be pre-determined but were identified in the field using a portable salinity probe (YSI, Inc.).

Water samples were acquired with 5 L Go-Flo bottles deployed on a Kevlar cable and triggered with a plastic messenger when the sampler was 1 m below the surface. After recovery, the bottle was pressurized with 8 psi nitrogen which forced the sample water through a pre-cleaned and

tared 142 mm diameter (0.4 µm pore-size) polycarbonate membrane held in a Teflon filter holder. The 142 mm filter was used for TSM determinations; an additional 250–500 ml were filtered through 47 mm (0.4 µm pore-size) polycarbonate membranes for particulate selenium speciation. All filter membranes were carefully folded, placed into polyethylene vials, and immediately frozen using dry-ice.

The water that passed through the filters was collected in 2-liter HDPE graduated cylinders and transferred to 1 L borosilicate bottles (Teflon-lined caps), acidified to pH 1.6 with HCl, and stored in the dark until analysis for selenium speciation. Filtered water was also placed into 125 mL borosilicate bottles for salinity/chlorinity determinations, and 125 mL polyethylene bottles for nutrient analyses. The nutrient samples were immediately frozen using dry-ice.

In addition, filtered samples were also collected for chlorophyll-a and phaeophytin-a using pre-cleaned (Whatman, GF/F) filters and particulate organic carbon and nitrogen using 13 mm GF/F filters; all were immediately frozen and stored in the dark using dry ice.

River Samples - Samples were collected from the San Joaquin River at Vernalis and in the Sacramento River at Freeport using a small aluminum hulled outboard boat and processed using the same procedures described above.

Sample Logs - Sample logs provided by Dr. Greg Cutter's laboratory at Old Dominion University (ODU) were used to record all station information, including:

- Station number
- Date and time
- Latitude and longitude
- Station depth
- Weather
- Sample depth
- Dissolved sample type and bottle number
- Particulate sample type, filter size and weight (if necessary), vial number and volume of sample processed.

The completed sample log were scanned and emailed to the laboratory at ODU at the time of sample shipment and are included in Appendix C of this report. Original copies of the sampling logs are kept at Tetra Tech's offices in Lafayette, California. All samples were packed in coolers or sample boxes, with the frozen samples packed in dry-ice and shipped via overnight courier under chain-of-custody to ODU. Copies of the completed chain-of-custody forms are provided in Appendix D.

All of these field methods are identical to those used by Greg Cutter's laboratory for San Francisco Bay sampling from 1986 onwards (Cutter, 1989; Cutter and San Diego-McGlone, 1990; Cutter and Cutter, 2004; Doblin et al., 2006), and have been optimized for taking representative and unaltered samples for the concentration and speciation of dissolved and particulate selenium. They have been used by many other labs, including the US Geological Survey, for selenium studies. The methods have been published in the peer-reviewed scientific literature (Cutter, 1978, 1982, 1983, 1985; Velinsky and Cutter, 1990).

Refinery Receiving Water Samples

Receiving water samples were collected from the center-line of each refinery's diffuser and from 10m up- and down-current of each diffuser's center-line.

All samples were processed using the methods described above.

Refinery Effluent Samples

Refinery effluent samples were collected monthly as 24 hour composites by each refinery's staff and placed into 2-liter polyethylene bottles. All samples were labeled and placed in a sealed sample storage location with filled-in chain-of-custody form for pick-up by Tetra Tech staff.

Samples were delivered to Pacific EcoRisk (Fairfield, CA) and processed by Tetra Tech and Pacific EcoRisk staff using the procedures described above for the transect water samples with the following modifications :

Modification 1 – To process samples for dissolved selenium speciation, the membrane filters used in the processing of the effluent samples were replaced with capsule filters (GWV High-Capacity Groundwater Sampling Capsules, Pall Life Sciences (3.2mm (1/8") MNPT Effective filtration area: 700 cm^2 (108-1/2 $in.^2$). Since the capsule filters were not designed for vacuum filtration, positive pressure using a peristaltic pump (MasterFlex) was used to collect the dissolved selenium fraction. This modification was made after the first sampling event (September 23–October 6, 2010).

Modification 2 – For the particulate speciation, samples need to be collected on membrane filters rather than the capsule filters using for processing the samples for dissolved selenium (above). High levels of particulates resulted in our being able to process only 200 ml per filter, rather than the 500 ml as described in the methods developed by Cutter. This resulted in multiple 47mm membrane filters being used to collect the particulate selenium fractions rather than the two as prescribed by the method. Communications with laboratory staff indicated that this modification was acceptable as long as each filter was placed into a separate, labeled vial.

Modification 3 – Filters were placed into a laboratory-grade freezer immediately after processing and allowed to freeze prior to shipping to the laboratory. All filters are shipped as described for the transect samples using dry-ice as a preservative.

Sample Issues

Several TSM samples from the 2011 wet weather event were compromised by what appears to be filter break-through during the filtration stage for these samples. While not apparent at the time of sample collection, filter weights were significantly lower in these samples, making it impossible to quantify TSM and particulate selenium concentrations. Several additional internal process assessments were performed to determine the cause of the filtration break-through and discussion of this issue is provided in Appendix E of this report.

3 Laboratory Analysis

Laboratory analyses followed the procedures described in Box 1 and presented in the Study Plan.

The only adjustment made to the original analytical methods was the use of a microwave-assisted digestion system for the determination of suspended total particulate selenium on polycarbonate filters. As a result, the 3-step nitric and perchloric acid digestion has been changed to a single step digestion that uses concentrated nitric acid and potassium persulfate over a 1.5 hour, 180° C period, followed by evaporation, and the addition of 2 mL of deionized water and evaporation. The addition of deionized water, followed by evaporation is repeated 2 times to remove all nitric acid. The resulting residue is taken up in 10 mL 6M hydrochloric acid and passed through AG1x8 resin to remove interfering iron (Box 1, paragraph II). This new digestion procedure was evaluated using digestions of NIST Standard Reference Materials 8704 (Buffalo River Sediment) and 1646A (Estuarine Sediment); full recoveries were found.

Box 1. Sample Analyses

I. The speciation of dissolved selenium will be determined using the selective hydride generation/atomic absorption detection method described by Cutter (1978; 1982; 1983). Briefly, within a glass stripping vessel selenite is quantitatively converted to hydrogen selenide using sodium borohydride addition to a sample containing sulfanilamide to eliminate interference due to nitrite and acidified to 4 mol l^{-1} HCl . The evolved hydrogen selenide is stripped from solution using helium and trapped in a borosilicate U-tube packed with silanized glass wool and immersed in liquid nitrogen. After the trap is removed from the LN_2, an atomic absorption spectrometer fitted with a open quartz tube furnace burning an air-hydrogen flame is used to detect the hydride; instrument response (as peak area) is recorded on a chromatographic integrator. To determine selenate+selenite, another acidified sample is boiled for 15 minutes, cooled, and then subjected to the selenite determination; selenate is the difference between this determination and that of selenite. Total dissolved selenium is determined by boiling a 4 mol l^{-1} HCl acidified sample, with the addition of potassium persulfate, and then following the selenite procedure. The difference between total dissolved selenium and selenite+selenate yields the concentration of dissolved organic selenide + elemental selenium (this may be colloidal and pass through the 0.4 µm filter). However, many studies have shown that this fraction is primarily organic selenide in the form of dissolved peptides (Cutter, 1982; Cutter and Bruland, 1984; Cutter and Cutter, 1995), and hereafter it is referred to as "dissolved organic selenide." To ensure accuracy, all determinations will utilize the standard additions method of calibration, and all samples will be analyzed in triplicate to quantify precision (found to be < 4% for concentrations above 0. 03 µg/l). Detection limits for all three selenium forms are 0.0016 µg/l.

II. The total selenium content of suspended particles and phytoplankton cultures will be determined using wet oxidative digestion followed by selective hydride generation atomic absorption spectroscopy (Cutter, 1978, 1983). Filters are dried at 40° C, weighed (for TSM concentration), and subsequently digested using a three step nitriCPerchloric acid reflux procedure (Cutter, 1985), but using an automated microwave digestion system with microwave-assisted evaporation. After evaporation of most of the nitric acid, the residue is redissolved in 4M HCl, passed through a column filled with Bio-Rad AG1 x 8 anion exchange resin (chloride form, 100–200 mesh) to remove iron and stored until final selenium analyses. Selective leaches will be conducted for determination of particulate selenium speciation (elemental selenium, Velinsky and Cutter 1990; SeIV + SeVI selenium, Cutter 1985). Aliquots of the digestion or selective leach solutions will be analyzed using the total dissolved selenium procedures of Cutter (1982, 1983). The standard additions method of calibration is used to ensure accuracy, and all determinations are made in triplicate. Accuracy will also be determined using the digestion and analysis of standard reference material (NIST 1566 or 1566b Oyster Tissue), for which recoveries will have to be within 1 standard deviation of the certified values to be accepted. The detection limit for particulate selenium is 0.0004 µg/l, with precision (as relative standard deviation) being better than 5%.

III. Filters for organic carbon and nitrogen analyses will be dried at 40° C and processed using a Elementar Micro-cube Elemental Analyzer (Cutter and Radford-Knoery, 1991). Chlorophyll-a will be extracted in 90% acetone in the dark at 4° C and determined using the fluorometric method of Strickland and Parsons (1972).

IV. The nutrients phosphate, silicate, and nitrate+nitrite will be determined using the colorimetric methods of Parsons et al. (1984), modified for use by an Astoria-Pacific rapid flow analyzer. Salinity is determined using a Portasal salinometer with IAPSO standard seawater as the reference.

4 Sampling Results

Results are presented for two categories of data: 1) dry and wet weather transect and refinery receiving water sampling, collected 4 times between September 2010 and April 2012, and 2) refinery effluent monthly sampling from September 2010 to August, 2011.

Because of the large volume of data collected, both the number of stations and the number of analytical values reported at each station, plots of key values are shown in this section, and actual values of reported data are presented in tabular form in Appendix B of this report. In the remainder of Section 4, the following approach has been used for the discussion of each type of data: first, specific tables containing data in Appendix B are identified, followed by a presentation of plots of data and associated findings for individual plots. The results are presented in this sequence:

- Dry weather transect data on ancillary parameters, dissolved Se species, particulate Se species (Section 4.1)
- Wet weather transect data on ancillary parameters, dissolved Se species, particulate Se species (Section 4.2)
- Dry weather receiving water samples including data on dissolved Se species and particulate Se species (Section 4.3)
- Wet weather receiving water samples including data on dissolved Se species and particulate Se species (Section 4.4)
- Summary of all transect data across wet and dry seasons (Section 4.5)
- Refinery effluent data on dissolved Se species and particulate Se species (Section 4.6)

As a guide to the location of the data tables in Appendix B, specific table numbers, data descriptions and page numbers for the data tables are summarized below:

4.1 Transect Samples (Dry Weather 2010 and 2011)

The results of the 2010 and 2011 dry weather field transect sampling are presented in tabular form in Appendix B. Tables B-1a, B-1b, B-2a, B-2b, B-3a and B-3b show dissolved and particulate selenium concentrations as well as concentrations of relevant ancillary parameters.

Tables B-1a and B-1b show the transect concentrations of the different dissolved selenium species analyzed in this work (selenate, selenite, organic selenium, and total dissolved selenium) for the 2010 and 2011 dry weather sampling events. Data for 2010 are reported for 21 stations in the estuary, with one sample that was lost due to breakage during shipping to the analytical laboratory; data for 2011 are reported for 24 stations in the estuary. Data are also reported for two stations that mark the major riverine boundary inputs into the Delta: Freeport on the Sacramento River, and Vernalis on the San Joaquin River. These stations can be used to define the watershed inputs of selenium with no influence from either the Delta or the estuary.

Tables B-2a and B-2b show the concentrations of relevant ancillary parameters in the dissolved phase for the 2010 and 2011 events, respectively. The ancillary parameters of interest in this study include key nutrient species (sum of nitrate and nitrite and phosphate), and silicate, a constituent essential for diatom growth. Also relevant to the cycling of selenium and uptake by filter feeding organisms are the chlorophyll a concentrations and total suspended material (TSM) concentrations.

Tables B-3a and B-3b show total particulate selenium data over the same transect and boundary locations for the 2010 and 2011 dry weather events. The salinity associated with the transect stations ranges from <1 psu to ~33 psu, reflecting conditions with minimal seawater influence at the western edge of the Delta to the stations close to seawater salinity.

In addition to the transect data, concentration data for samples collected in the vicinity of the five refinery outfalls are shown in Tables B-4a and B-4b. As mentioned previously, the objective of this sampling was to characterize the mixing characteristics of the discharge and the speciation of the selenium upon initial dilution in the receiving water. Samples were collected from the outfall of each refinery's diffuser as well as from two additional locations approximately 10m to either side of the diffuser center-line in order to capture the upstream and downstream selenium concentrations, for a total of three stations per refinery. Total dissolved selenium and particulate total selenium concentrations were quantified at each station. The tide stage, station depth and sample depth for each refinery during the 2010 and 2011 sampling events are provided in Tables B-5a and B-5b. Also identified is the relative location of the station to the outfall, whether it is upstream of downstream of it.

The results presented in these tables are discussed below using plots of concentrations along the estuary and also compared with prior measurements.

Ancillary Parameters

Spatial trends for the ancillary parameters in the 2010 and 2011 dry season sampling events, as well as comparisons with the 1999 dry weather sampling are shown in Figure 4-1 through Figure 4-6. For the 2011 dry season sampling, only TSM data were available. Patterns in individual constituents are discussed below.

- Figure 4-1 shows nitrite and nitrate concentrations in the estuary and at the boundary stations. Concentrations in San Joaquin River are nearly sixty times higher than in Sacramento River, and estuarine concentrations are about 20 µmol/liter. Estuarine concentrations are much higher than Sacramento River concentrations and exhibit a gradual decline from the freshwater to the seawater end. Concentrations in 2010 are broadly in the same range as the 1999 values, although concentrations in 2011 are consistently lower.
- Phosphate concentrations are shown in Figure 4-2, and display a narrower range between the estuary and boundary stations than do the nitrite plus nitrate concentrations. Concentrations are higher in the San Joaquin River by a factor of about three, and concentrations in the estuary are similar to those in the Sacramento River. Concentrations are about 50% higher in the 2010 sampling than in 1999 and 2011.
- Silicate concentrations in the rivers and the estuary are shown in Figure 4-3. Concentrations in the two rivers are much nearer one another than the nutrient concentrations, and overall, the estuary shows a strong decline toward the seawater end. Concentrations are about 50% lower in 2010/2011 than in 1999.

- Chlorophyll a concentrations during the 2010 sampling were similar but slightly lower than concentrations observed during the 1999 sampling, ranging from 0.5–2.0 µg/L (Figure 4-4). Concentrations at the seawater end of the estuary are often high, especially in the 2011 sampling.
- TSM concentrations include both inorganic and organic material, and consist of riverine inputs, as well as material resulting from planktonic productivity in the estuary. TSM concentrations exhibited interesting patterns spatially and when the three dates of sampling were compared (Figure 4-5). In the 1999 and 2011 sampling, concentrations decreased with increasing salinity, indicating a settling of riverine particulates. In the 2010 sampling, concentrations increased with salinity. Concentrations exhibited a decline near the Golden Gate stations for all sampling periods.
- Consistent with Figure 4-5, the ratio of chlorophyll a to TSM (representing the living versus the non-living fraction of this constituent) was lower in 2010 than 1999 and 2011 for most samples collected in the estuary, due to higher TSM and lower chlorophyll a observed in 2010 (Figure 4-6).

Taken together, the results of the ancillary sampling indicate a particulate mix in 2011 that was similar to that in 1999, with much higher particulate concentrations observed in 2010.

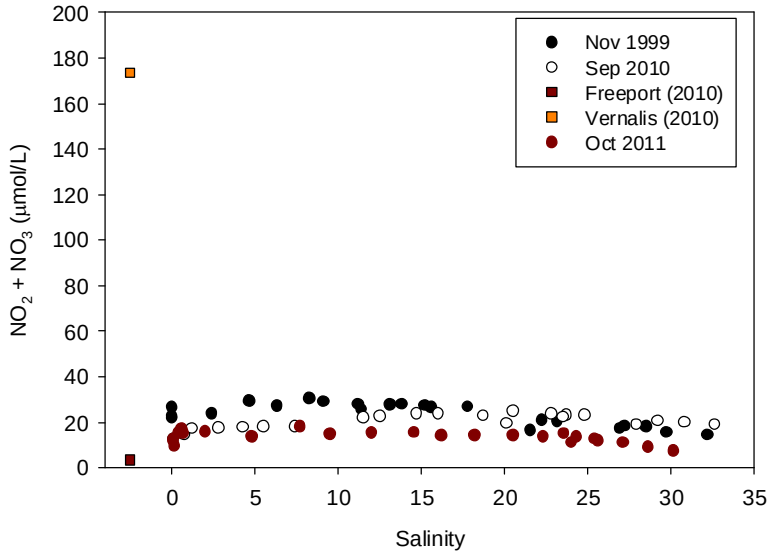

Figure 4-1
Dry weather concentrations of nitrite plus nitrate across the estuary with data from November 1999 and September 2010 and data from the riverine sources at Freeport (Sacramento River) and Vernalis (San Joaquin River).

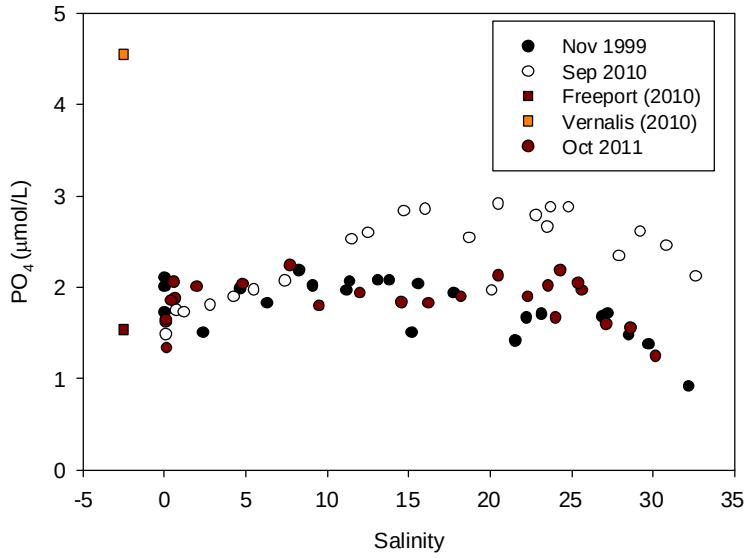

Figure 4-2
Dry weather concentrations of phosphate across the estuary with data from November 1999 and September 2010 and data from the riverine sources at Freeport (Sacramento River) and Vernalis (San Joaquin River).

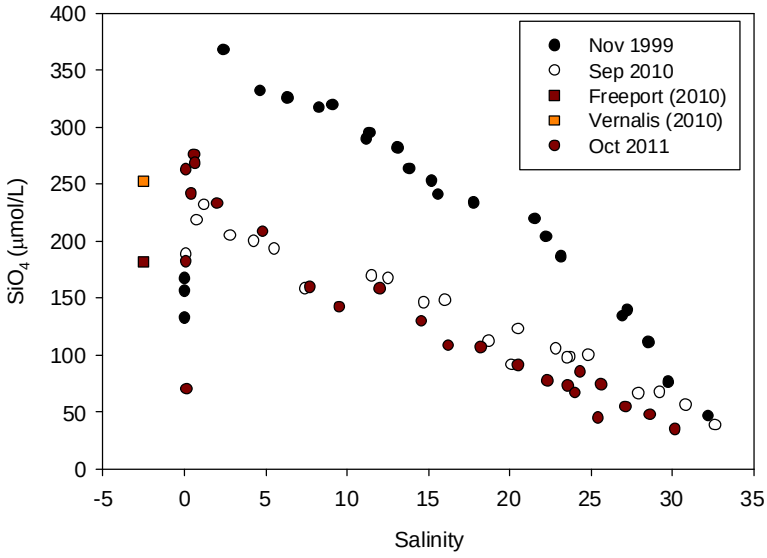

Figure 4-3
Dry weather concentrations of silicate across the estuary with data from November 1999 and September 2010 and data from the riverine sources at Freeport (Sacramento River) and Vernalis (San Joaquin River).

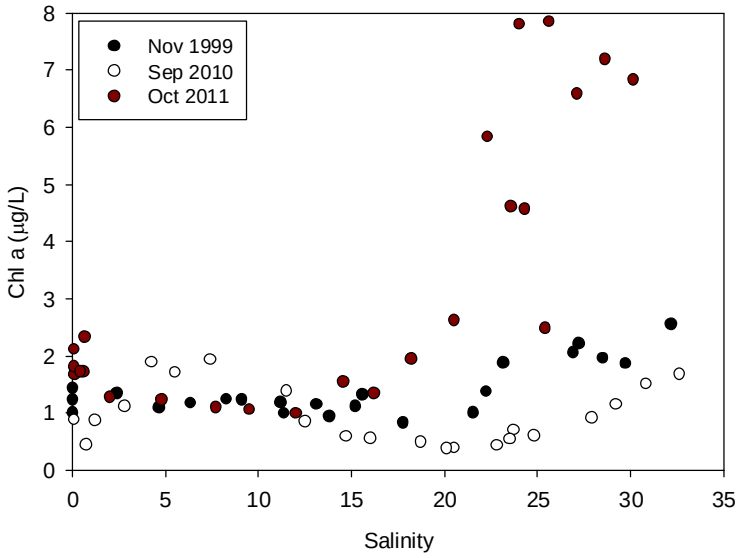

Figure 4-4
Dry weather concentrations of chlorophyll a across the estuary with data from November 1999, September 2010 (Data for river stations were not collected).

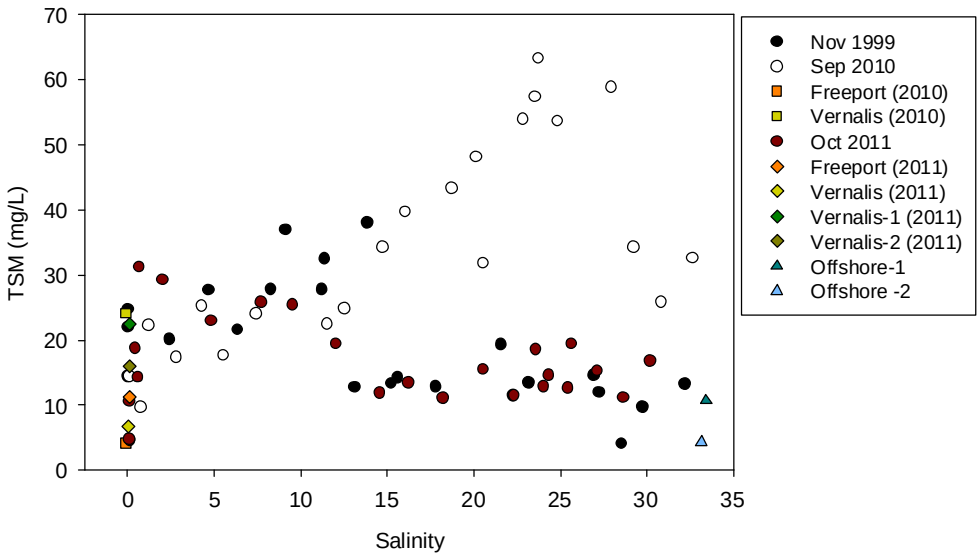

Figure 4-5
Dry weather concentrations of total suspended material (TSM) across the estuary with data from November 1999, September 2010 and October 2011. Also shown are 2010 and 2011 data from the riverine sources at Freeport (Sacramento River) and at Vernalis (San Joaquin River).

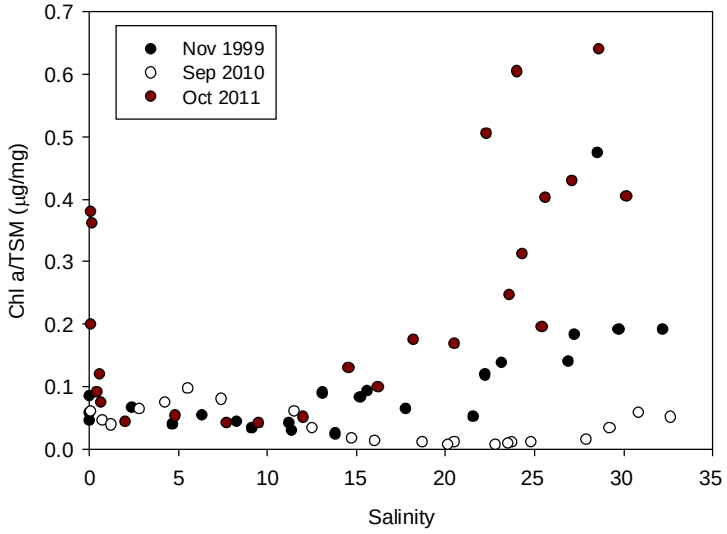

Figure 4-6
Ratio of chlorophyll a to TSM across the estuary with data from November 1999 and September 2010 (Data for river stations were not collected).

Dissolved Selenium Species

Concentrations of different selenium species through the estuary transect are presented in Figure 4-7 through Figure 4-10, and discussed individually below. The species are presented in the following order: selenite (SeIV), selenate (SeVI), organic selenide (Se-II), and dissolved selenium.

- Selenite data in the dissolved phase are shown along the estuary and the river stations in Figure 4-7. Concentrations are slightly higher in the estuary than in the riverine inputs, with the highest concentrations in the mid-salinity regions of the bay. There is a decrease in concentrations toward the Golden Gate, with offshore concentrations lower than the estuarine concentrations. The three periods of sampling are broadly consistent, with the 2010 and 2011 values being higher the 1999 values in the mid-salinity portion of the estuary.
- Selenate data in the dissolved phase are shown in Figure 4-8. For this species, the riverine concentrations from Vernalis (San Joaquin River) are distinctly higher than estuary concentrations. However concentrations at Freeport (Sacramento River) are lower by a factor of 5, and lower than the estuary concentrations. Spatially, there is a slight increase in concentration in the mid salinity regions in 1999, but this is not noticeable for 2010 and 2011. There is a difference between the 1999 and 2010 sampling, with concentrations nearly half of their 1999 values at several stations throughout the bay. However, 2011 values are closer to the 1999 values. Selenate concentrations in the coastal stations are at approximately the same levels as the estuarine values in 2010 and 2011. Overall, selenate concentrations in 2010 are about twice the selenite concentrations shown in Figure 4-7.
- Selenide (organic selenium, or Se(-II)) concentrations are shown in Figure 4-9 and are considerably variable compared to the selenite and selenate values. There are greater similarities between the 1999 and 2011 sampling than the 2010 and 2011 sampling. Selenide concentrations were lower in the 1999 and 2011 sampling efforts compared to

2010. Spatially, concentrations exhibit a slight increase from the freshwater end to the Central Bay, and decrease near Golden Gate. The offshore values are lower than the estuarine values. In the 2010 sampling, selenide and selenate concentrations are of similar magnitude (about 0.04 µg/l). The riverine concentrations of selenide are not higher than the estuarine concentrations for both the Freeport and Vernalis locations.

- Despite the differences in individual species concentrations in 1999, 2010, and 2011 total selenium concentrations (Figure 4-10) for the three periods are quite similar, with slightly higher concentrations in the mid-salinity range, and lower and higher concentrations at the freshwater and seawater ends. The riverine boundary concentrations shown in this figure illustrate the difference between the Sacramento and San Joaquin River inflows. Concentrations in Vernalis are about 7 times greater than at Freeport. The coastal station concentrations are roughly in line with concentrations at Golden Gate, and at levels similar to the freshwater end of the estuary.

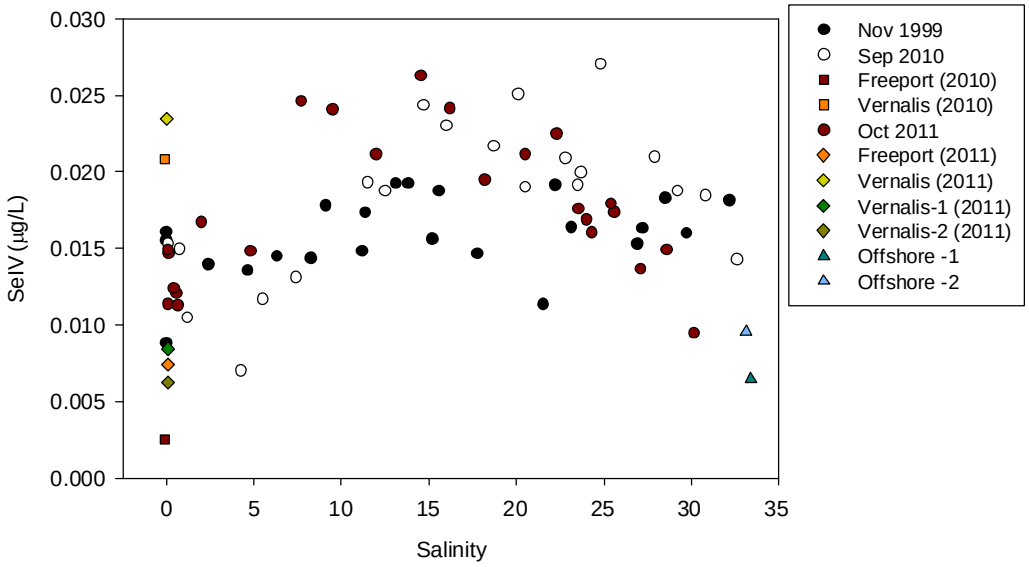

Figure 4-7
Dry weather selenite (SeIV) concentrations across the estuary with data from November 1999, September 2010 and October 2011. Also shown are SeIV concentrations sampled in the riverine sources at Freeport (Sacramento River) and Vernalis (San Joaquin River) as well as from two offshore locations.

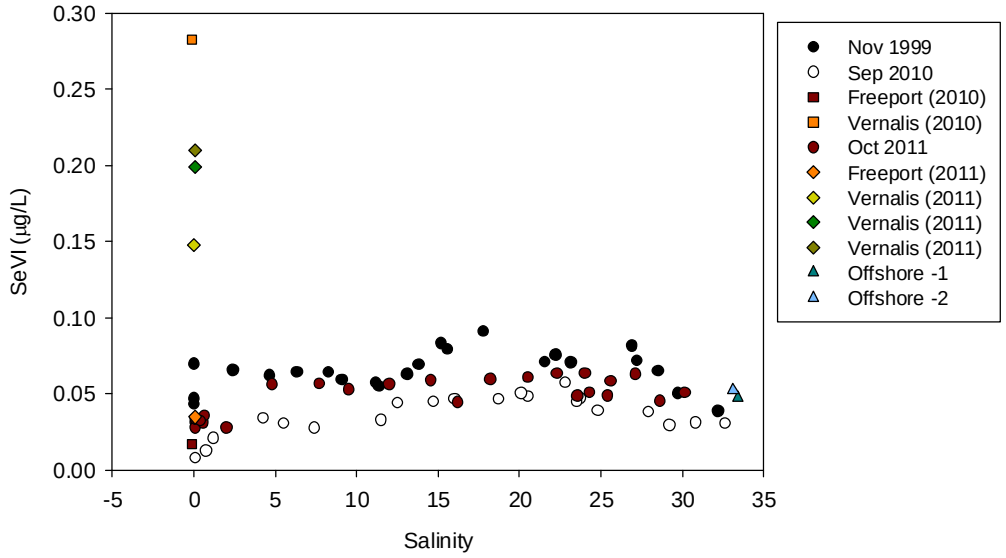

Figure 4-8
Dry weather selenate (SeVI) concentrations across the estuary with data from November 1999, September 2010 and October 2011. Also shown are SeVI concentrations sampled in the riverine sources at Freeport (Sacramento River) and Vernalis (San Joaquin River) as well as from two offshore locations.

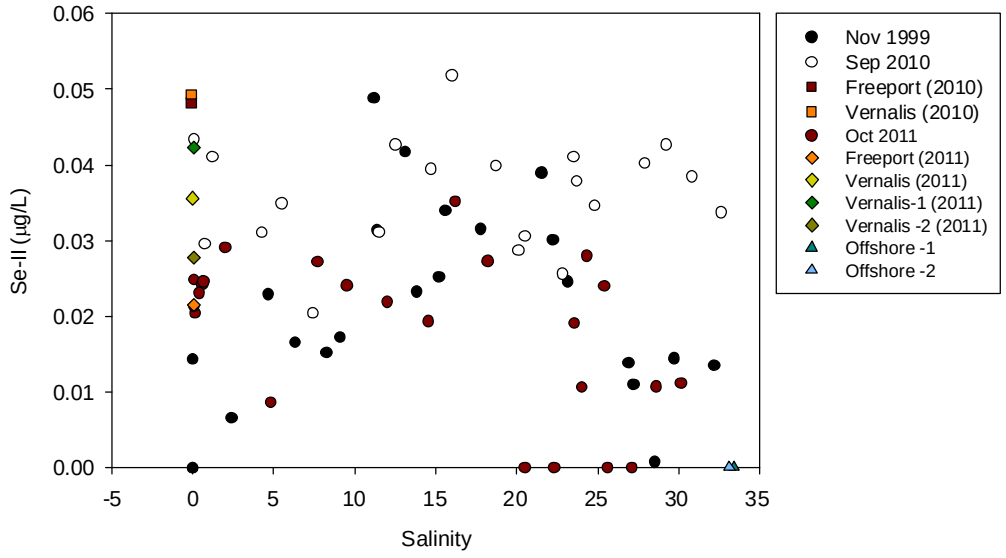

Figure 4-9
Dry weather organic selenium (Se-II) concentrations across the estuary with data from November 1999, September 2010 and October 2011. Also shown are Se-II concentrations sampled in the riverine sources at Freeport (Sacramento River) and Vernalis (San Joaquin River) as well as from two offshore locations.

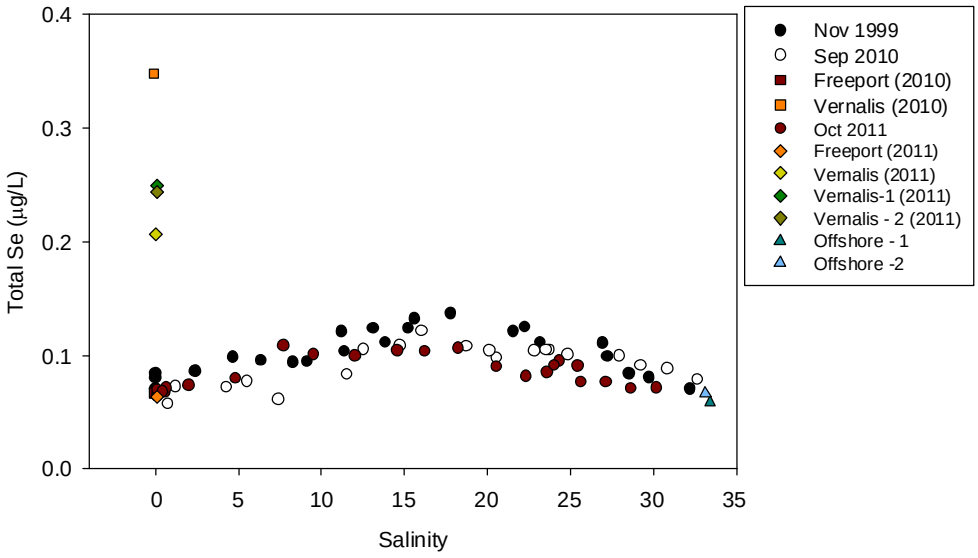

Figure 4-10
Dry weather total dissolved selenium concentrations across the estuary with data from November 1999, September 2010 and October 2011. Also shown are concentrations sampled in the riverine sources at Freeport (Sacramento River) and Vernalis (San Joaquin River) as well as from two offshore locations.

Particulate Selenium Species

Total particulate selenium concentrations across the estuary (shown as µg/g) and riverine/coastal boundary sites, are shown in Figure 4-11. Particulate selenium concentrations appear to be systematically lower in 2010 than in 1999 or 2011, especially for salinities above 10 g/L. Concentrations in the bay are lower than observed in the riverine inputs for San Joaquin and Sacramento Rivers. Concentrations in the Sacramento River are approximately half the concentrations in the San Joaquin River. For the 1999 and 2011 sampling events, there was an increase in concentrations across the estuary with relatively high concentrations observed near Golden Gate. Coastal concentrations of particulate selenium were also high, and averaged across two samples, higher than the estuary concentrations in 2011.

The ratio of the particulate to dissolved selenium concentrations, expressed as a Kd in units of l/g[1], across the estuary and the riverine boundaries, are shown in Figure 4-12. As with several particle associated measurements (TSM, total particulate Se), the 1999 and 2011 values are more similar than the 2010 values. In particular, there is a clear increase in Kd in the 1999 and 2011 observations. Importantly, Kd values in the coastal areas are higher than observed in the estuary. Kd values are higher in the Sacramento River than San Joaquin River by a factor of about 3, the values at the low salinity end of the estuary are similar to the Sacramento River values. The refinery values are about the same as or slightly lower than the estuary values at nearby locations.

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

Particulate selenium species including adsorbed selenite and selenate, elemental selenium and organic selenide were also sampled during September 2010 and October 2011 (Figure 4-13through Figure 4-15). Particulate elemental selenium concentrations were highest in 2010, and lower in 1999 and 2011, likely indicating the role of resuspended sediments (Figure 4-13). Particulate adsorbed selenite and selenate concentrations sampled in September 2010 were lower compared to 1999 and 2011 (Figure 4-14), a pattern that is the opposite of the elemental selenium concentrations. Particulate organic selenide concentrations were highly variable through the estuary, with somewhat higher concentrations observed in 2010 than in the other two years (Figure 4-15). For particulate organic selenide, concentrations at the riverine boundaries (San Joaquin River at the Vernalis and Sacramento River at the Freeport) are similar to the estuary transect, with concentrations within the estuary showing larger variations. Both particulate elemental and organic selenium concentrations showed large variations within the estuary. On average, particulate selenium concentrations were 12.5% of the dissolved selenium concentrations or 11.1% of the total selenium in the estuary.

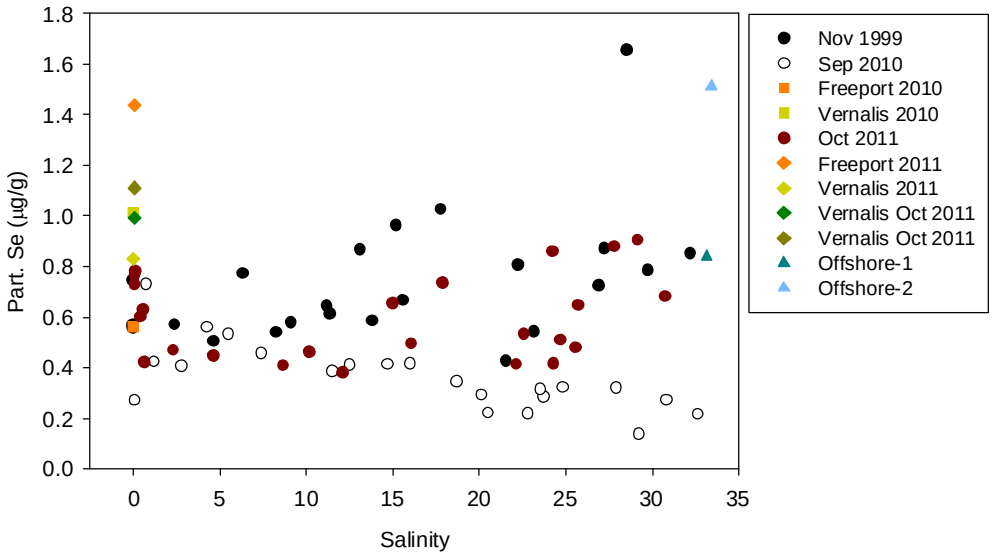

Figure 4-11
Dry weather total particulate selenium concentrations across the estuary with data from November 1999, September 2010 and October 2011. Also shown are concentrations sampled in the riverine sources at Freeport (Sacramento River) and Vernalis (San Joaquin River) as well as from two offshore locations.

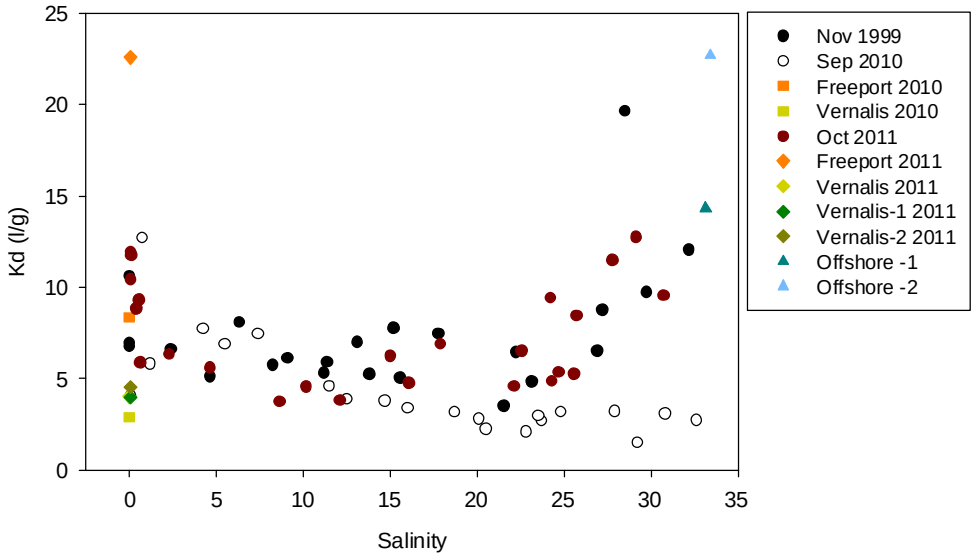

Figure 4-12
Ratio of particulate to dissolved selenium concentrations (expressed as Kd with units of l/g) across the estuary with data from November 1999, September 2010 and October 2011. Also shown are concentrations sampled in the riverine sources at Freeport (Sacramento River) and Vernalis (San Joaquin River) as well as from two offshore locations.

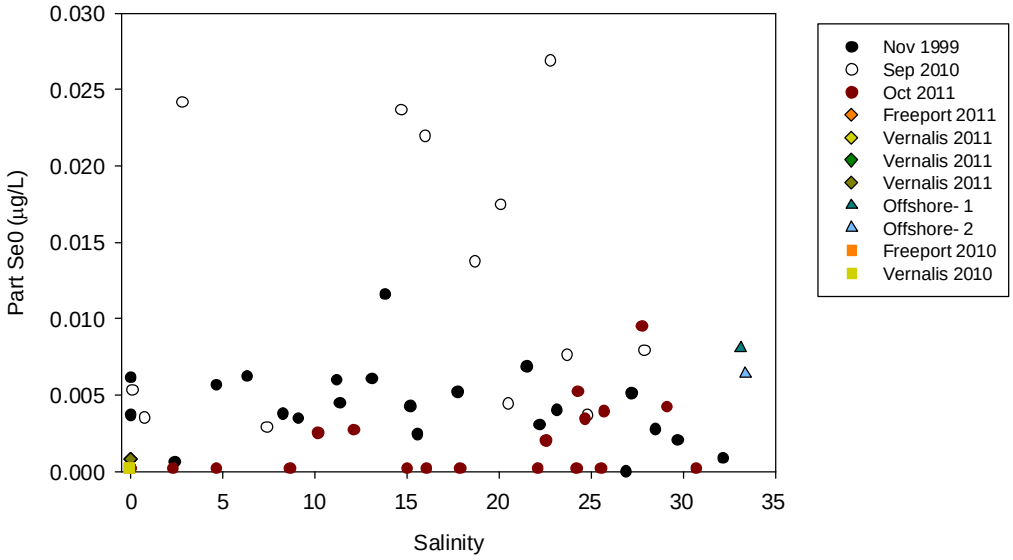

Figure 4-13
Dry weather particulate elemental selenium (Se0) concentrations in NSFB sampled during November 1999, September 2010, and October 2011.

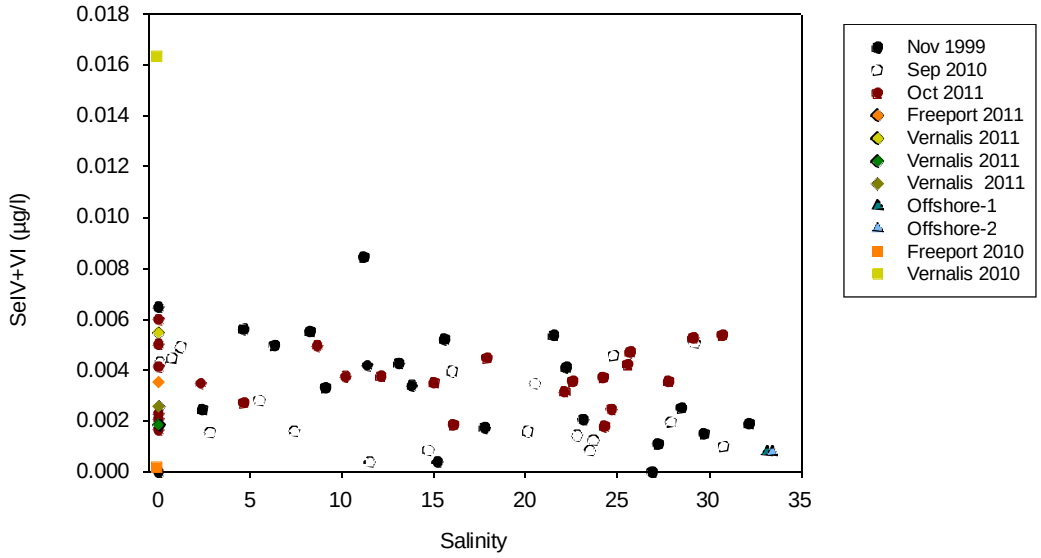

Figure 4-14
Particulate adsorbed selenite + selenate concentrations sampled in NSFB during November 1999, September 2010, and October 2011.

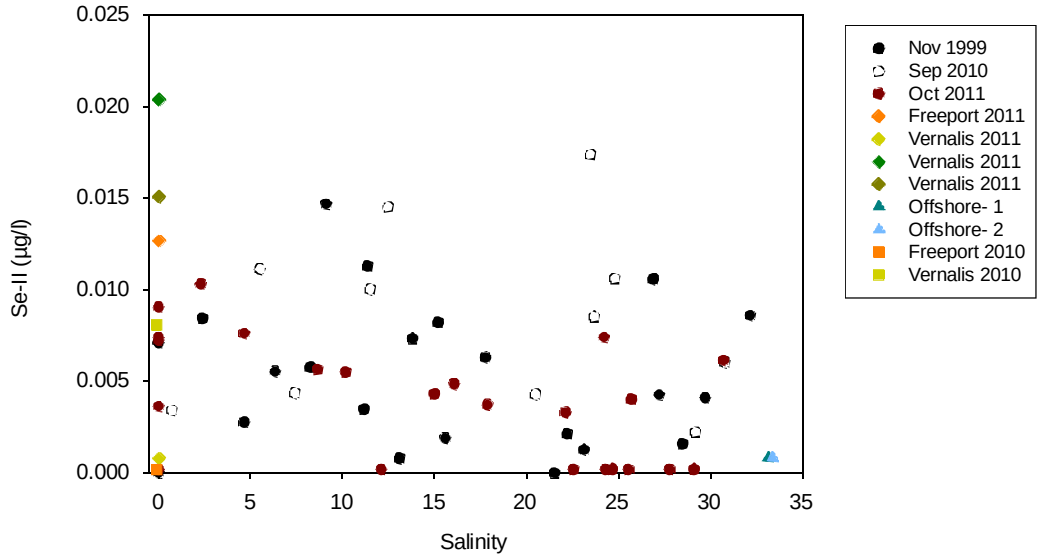

Figure 4-15
Particulate adsorbed organic selenide concentrations sampled in NSFB during November 1999, September 2010, and October 2011.

4.2 Transect Samples (Wet Weather, 2011–2012)

The results of the March 2011 and April 2012 field transect sampling are presented in Tables B-6a, B-6b, B-7a, B-7b, B-8a, B-8b, B-9a and B-9b for dissolved and particulate selenium concentrations and relevant ancillary parameters.

Tables B-6a and B-6b show the 2011 and 2012 wet weather transect concentrations of the different dissolved selenium species analyzed in this work (selenate, selenite, organic selenium, and total dissolved selenium). Data are reported for 20 and 21 stations in the estuary during the 2011 and 2012 wet weather events, respectively. Data are also reported for two stations that mark the major riverine boundary inputs into the Delta, i.e., Freeport on Sacramento River, and Vernalis on San Joaquin River. Tables B-7a and B-7b show the concentrations of relevant ancillary parameters in the dissolved phase. Tables B-8a and B-8b show total particulate selenium data over the same transect and at boundary locations. Chlorophyll a was not reported for the 2012 sampling event. The salinity associated with the transect stations ranges from <1 psu to ~28 psu, reflecting conditions with minimal seawater influence at the western edge of the Delta to the stations close to seawater salinity. Selenium concentrations measured along the transect can be directly compared to a previous set of measurements, made using virtually identical analytical methods, and by the same laboratory in 1999 (reported in Cutter and Cutter, 2004 and Doblin et al., 2006). Field blank concentrations for this set of samples are high, and exceed any individual sample value. The cause of this exceedance is not known, although as described later, most of the concentration numbers in this set of data are broadly comparable to previous measurements (in 1999 and in 2010), thus indicating that no systematic error occurred.

In addition to the transect data, concentration data for samples collected in the vicinity of the five refinery outfalls are shown in Tables B-9a and B-9b. As mentioned previously, the objective of this sampling was to characterize the mixing characteristics of the discharge and the speciation of the selenium upon initial dilution in the receiving water. Samples were collected from the outfall of each refinery's diffuser as well as from two additional locations approximately 10 m to either side of the diffuser center-line in order to capture the upstream and downstream selenium concentrations, for a total of three stations per refinery. Total dissolved selenium and particulate total selenium concentrations were quantified at each station. The expectation was that during ebb and flood tides, the highest concentrations would be found at the centerline, lowest concentrations upstream, and intermediate concentrations downstream. Concentrations would be relatively similar at the upstream and downstream sites and elevated at centerline stations during slack tides. The tide stage, station depth and sample depth for each refinery during sampling is provided in Table B-10. Also identified is the relative location of the station to the outfall, whether it is upstream of downstream of it.

Ancillary Parameters

Spatial trends for the ancillary parameters in the 2011 and 2012 wet season sampling, as well as comparisons with the 1999 wet weather sampling are shown in Figure 4-16 through Figure 4-21. Patterns in individual constituents are discussed below.

- Figure 4-16 shows nitrite and nitrate concentrations in the estuary for the April 1999, March 2011, and April 2012 sampling. Concentrations are broadly similar over the three sampling periods and show a decreasing trend toward Golden Gate. Vernalis concentrations are about ten-fold higher than Freeport concentrations.
- Phosphate concentrations are shown in Figure 4-17. Phosphate concentrations in the estuary are in the same range as the riverine concentrations (unlike the nitrite plus nitrate concentrations). Vernalis concentrations are higher than Freeport concentrations but not as

elevated as for the nitrite plus nitrate values. Within the estuary concentrations are slightly higher in the mid-salinity range and decline toward the seaward end.

- Silicate concentrations in the estuary are shown in Figure 4-18 for the April 1999, March 2011, and April 2012 sampling. Silicate concentrations show a relatively strong linear decline toward the seawater end for all three periods. Concentrations are very similar across the three sampling periods.
- Chlorophyll a concentrations during the March 2011 sampling are lower than the April 1999/April 2012 values (Figure 4-19). The observed pattern is similar to observations for the dry weather sampling, in which higher chlorophyll a concentrations were found in 2010 sampling compared to previous sampling of November 1999. Higher chlorophyll a concentrations may be caused by several factors such as phytoplankton blooms, decreases in grazing, or a shift in algal species.
- TSM concentrations exhibited interesting patterns spatially over the estuary and also when the three dates of sampling were compared (Figure 4-20). The 1999 sampling shows an estuarine turbidity maximum at a salinity of 7.5 psu, with TSM concentrations decreasing toward the seaward end. This pattern was also noted in the April 2012 sampling. The 2011 sampling, however, showed increases in TSM concentrations toward the seaward end. One possible explanation of the increases in TSM is possibly the high turbidity near the Central Bay, imposed by either South Bay water or greater planktonic production. The riverine concentrations of TSM, particularly in the Sacramento River, were in the same range as the estuarine concentrations.
- Consistent with Figure 4-20, the ratio of chlorophyll a to TSM (representing the living versus the non-living fraction of this constituent) was lower in March 2011 than April 1999/April 2012 (Figure 4-21).

Taken together, the results of the ancillary sampling in March 2011 and April 2012 show similar results for nitrite plus nitrate and silica concentrations. There is more scatter in the other parameters, with April 1999 values being more similar to April 2012 values than March 2011 values.

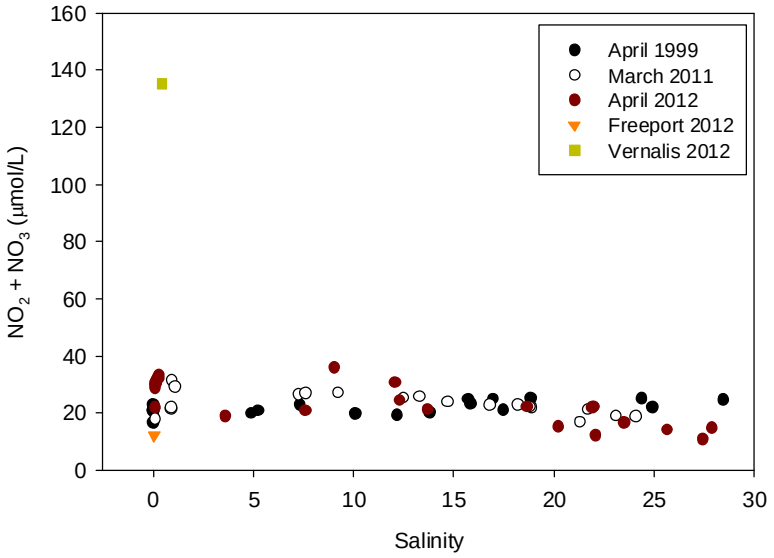

Figure 4-16
Wet weather concentrations of nitrite plus nitrate across the estuary with data from April 1999, March 2011 and April 2012. Also shown are concentrations sampled in the riverine sources at Freeport (Sacramento River) and Vernalis (San Joaquin River).

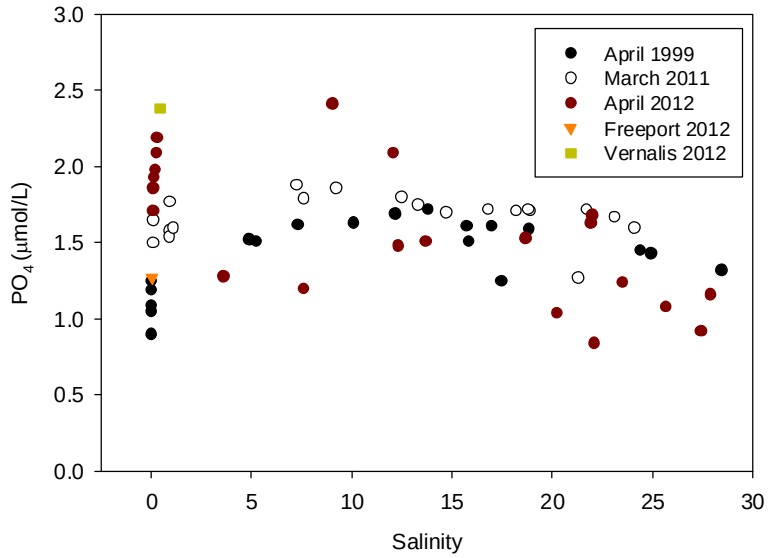

Figure 4-17
Wet weather concentrations of phosphate across the estuary with data from April 1999, March 2011 and April 2012. Also shown are concentrations sampled in the riverine sources at Freeport (Sacramento River) and Vernalis (San Joaquin River).

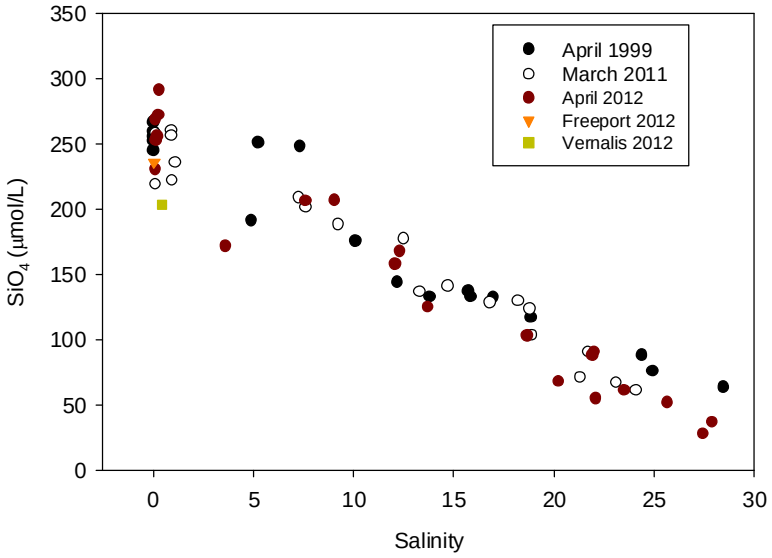

Figure 4-18
Wet weather concentrations of silicate across the estuary with data from April 1999, March 2011 and April 2012. Also shown are concentrations sampled in the riverine sources at Freeport (Sacramento River) and Vernalis (San Joaquin River).

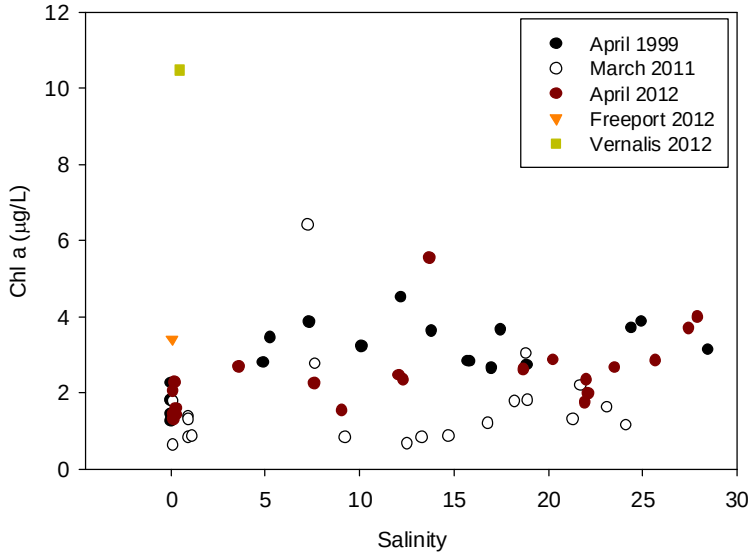

Figure 4-19
Wet weather concentrations of chlorophyll a across the estuary with data from April 1999 and March 2011.

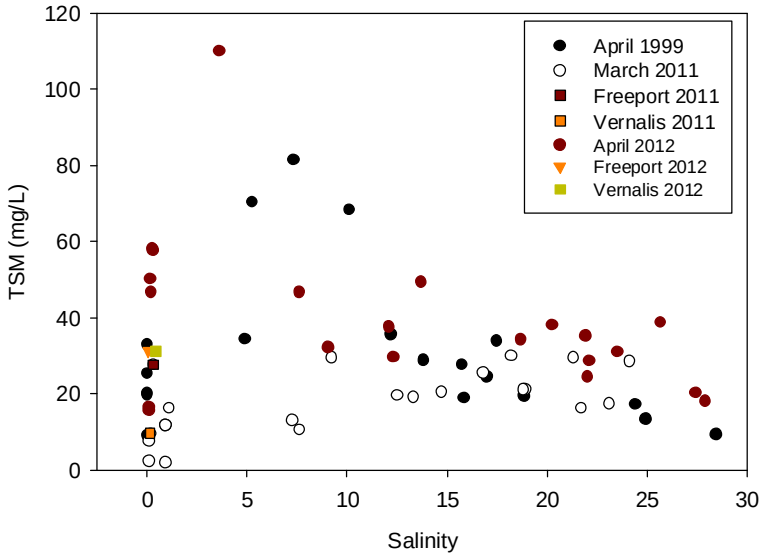

Figure 4-20
Wet weather concentrations of total suspended material (TSM) across the estuary with data from April 1999, March 2011 and April 2012. Also shown are data from the riverine sources at Freeport (Sacramento River) and at Vernalis (San Joaquin River).

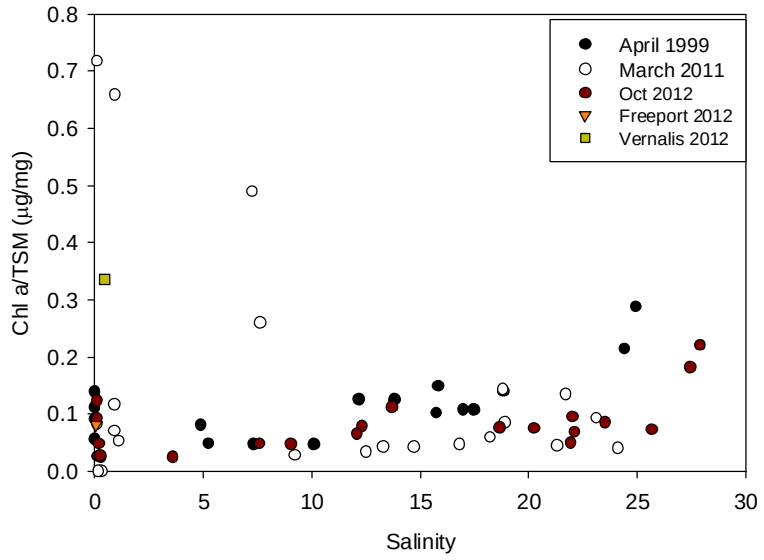

Figure 4-21
Ratio of chlorophyll a to TSM across the estuary with data from April 1999 and March 2011. Chlorophyll-a data were not available for April 2012.

Dissolved Selenium Species

Concentrations of different selenium species through the estuary transect are presented in Figure 4-22 through Figure 4-25, and discussed individually below.

- Selenite data in the dissolved phase are shown along the estuary in Figure 4-22. Concentrations are higher in March 2011/April 2012 than in April 1999. Of the three sampling periods, the April 2012 values show an increase toward the seaward end. The riverine boundary of Sacramento River at Freeport shows lower concentrations than the estuary. In comparison, concentrations at Vernalis are about two to three times as high as the selenite concentrations at the head of the estuary.
- Selenate data in the dissolved phase are shown in Figure 4-23. For this species, concentrations showed a slight decrease toward the seaward end. Concentrations from the March 2011/April 2012 sampling are similar to the April 1999 data. Selenate concentrations from San Joaquin River at Vernalis were about six times higher than the estuarine concentrations near the head of the estuary and concentrations from the Sacramento River at Freeport were in the range of the estuarine concentrations.
- Selenide (organic selenium, or Se(-II)) concentrations are shown in Figure 4-24 and are considerably variable along the transect. The variation is likely due to variations in phytoplankton exhibited in the estuary. The selenide concentrations observed in April 1999 were higher than the 2011/2012 values.
- Total dissolved selenium concentrations (Figure 4-25) for the three sampling periods are similar, with concentrations showing a marginal decline toward the seaward end. The riverine boundary concentrations are different between the Sacramento and the San Joaquin Rivers. Concentrations in San Joaquin River at Vernalis are about 3-5 times greater than at Freeport.
- Dissolved selenium concentrations in the estuary were in-between the two riverine boundary concentrations. It appears that dissolved selenium concentrations in the estuary are closer to the Sacramento River samples at Freeport. The same pattern was observed during the dry weather sampling reported earlier.

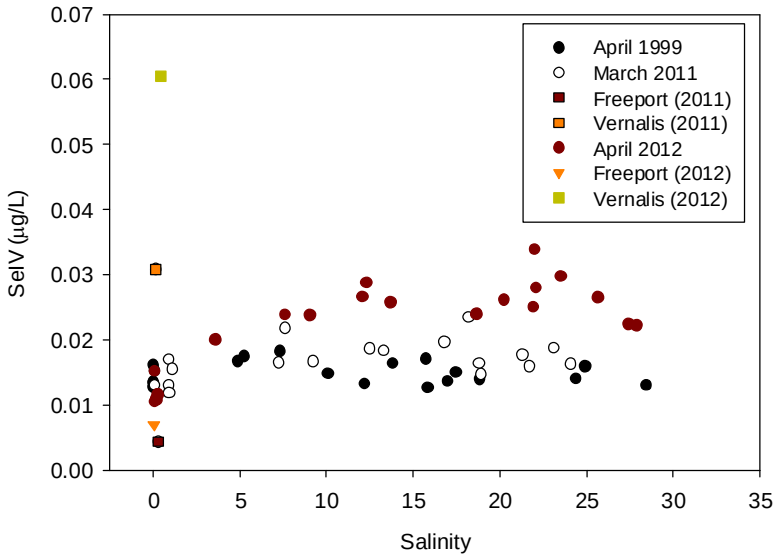

Figure 4-22
Wet weather selenite (SeIV) concentrations across the estuary with data from April 1999, March 2011 and April 2012. Also shown are selenite concentrations sampled in the riverine sites at Freeport (Sacramento River) and Vernalis (San Joaquin River).

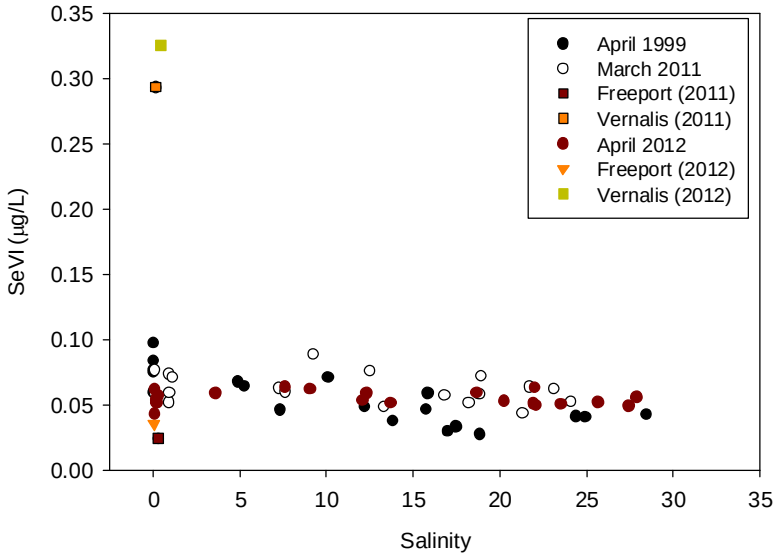

Figure 4-23
Wet weather selenate (SeVI) concentrations across the estuary with data from April 1999, March 2011 and April 2012. Also shown are selenite concentrations sampled in the riverine sites at Freeport (Sacramento River) and Vernalis (San Joaquin River).

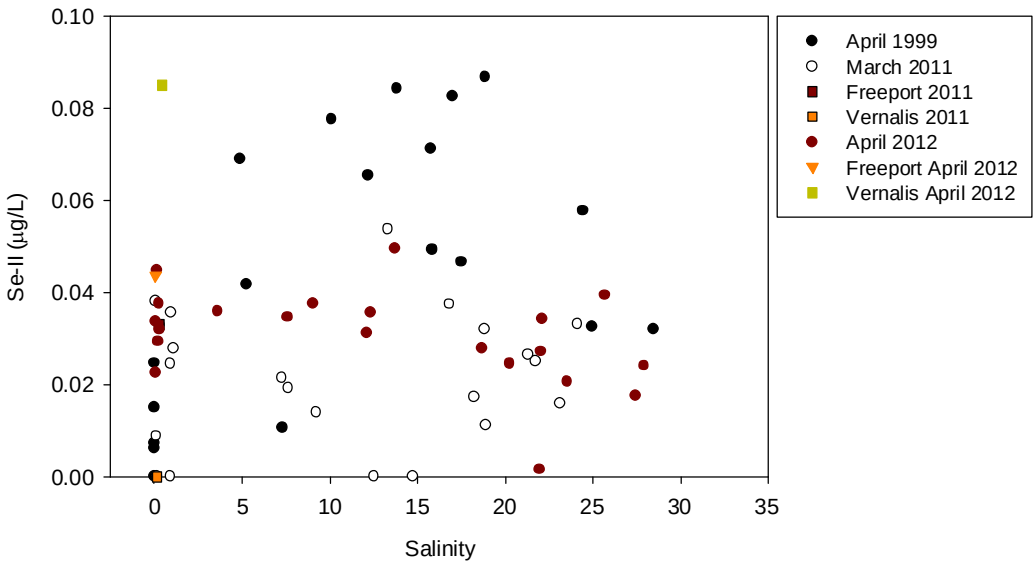

Figure 4-24
Wet weather organic selenium (Se-II) concentrations across the estuary with data from April 1999, March 2011 and April 2012. Also shown are selenite concentrations sampled in the riverine sites at Freeport (Sacramento River) and Vernalis (San Joaquin River).

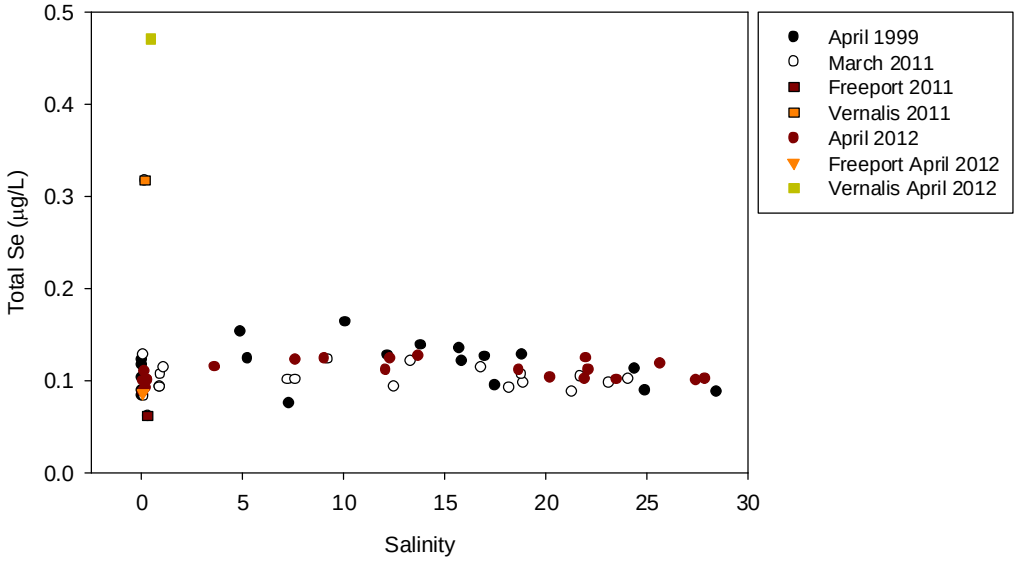

Figure 4-25
Wet weather total dissolved selenium concentrations across the estuary with data from April 1999, March 2011 and March 2012. Also shown are data from the riverine sources at Freeport (Sacramento River) and at Vernalis (San Joaquin River).

Particulate Selenium Species

Total particulate selenium concentrations across the estuary (shown as µg/g), including the riverine boundary sites, are shown in Figure 4-26. All data are shown in the plots in this section, although based on additional sampling, data from four low-TSM locations (T-13, T-14, T-17, and the Vernalis station on San Joaquin) were flagged for subsequent modeling analysis. Particulate concentrations were slightly lower in 2011 compared to 1999 and 2012 values. In addition, some high particulate selenium concentrations (shown as µg/g) were found at stations near the head of the estuary (>1.5 µg/g). These stations are associated with high chlorophyll a/TSM ratios. Particulate selenium concentrations in the bay are generally lower than the riverine concentrations at the San Joaquin and the Sacramento Rivers.

The ratio of particulate to dissolved selenium concentrations, expressed as a Kd in units of l/g, across the estuary, including the riverine boundary and refinery outfall sites, are shown in Figure 4-27. Kd values sampled during high flow are similar between 1999, 2011 and 2012. Some high Kd values were found at the head of the estuary stations. Kd values are higher in the Sacramento River than the San Joaquin River by a factor of about 3. The values at the low salinity end of the estuary are similar to the Sacramento River values.

Particulate selenium species including particulate adsorbed selenite and selenate, particulate elemental selenium and particulate organic selenide were sampled during March 2011 and April 2012. Particulate adsorbed selenite and selenate concentrations (expressed in µg/L) sampled in March 2011/April 2012 were similar to the 1999 samples (Figure 4-28). Concentrations from riverine stations are very similar to estuarine concentrations. In contrast, particulate elemental selenium concentrations in March 2011and April 2012 are mostly non-detect (Figure 4-29).

Particulate selenium speciation was dominated by adsorbed selenite and selenate and organic selenide. Compared to the sampling in April 1999, the most noticeable changes in the recent particulate selenium speciation are decreases in particulate elemental selenium. The lack of

particulate elemental selenium suggests minimal contribution of bed sediments to the TSM sampled in March 2011 and April 2012.

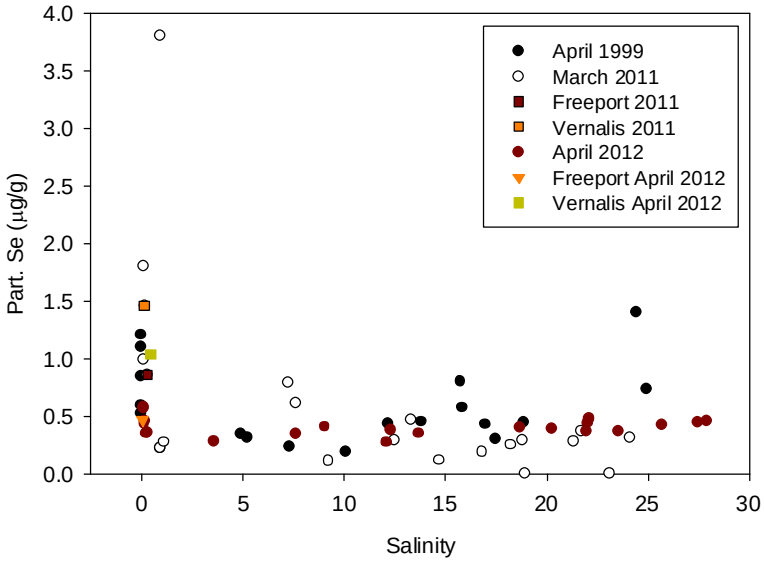

Figure 4-26
Wet weather total particulate selenium concentrations across the estuary with data from April 1999, March 2011 and March 2012. Also shown are data from the riverine sources at Freeport (Sacramento River) and at Vernalis (San Joaquin River).

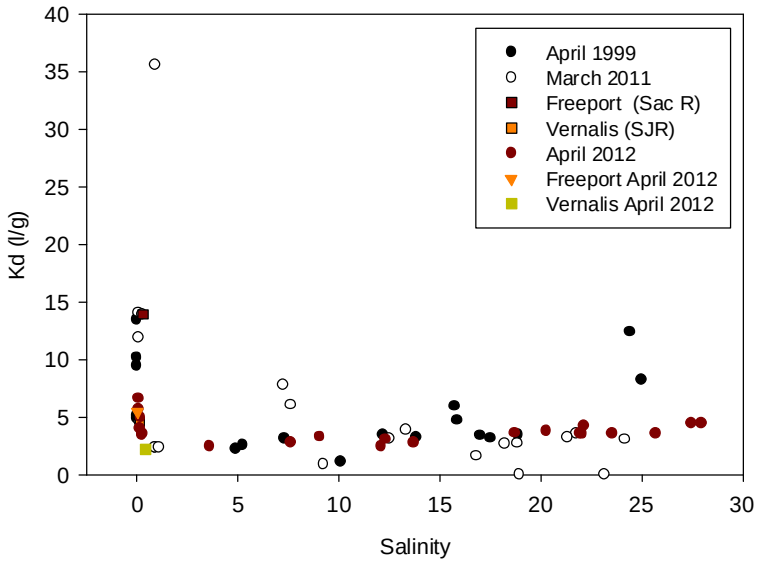

Figure 4-27
Ratio of particulate to dissolved selenium concentrations (expressed as Kd with units of l/g) across the estuary with data from April 1999, March 2011 and April 2012. Also shown are data from the riverine sources at Freeport (Sacramento River) and at Vernalis (San Joaquin River).

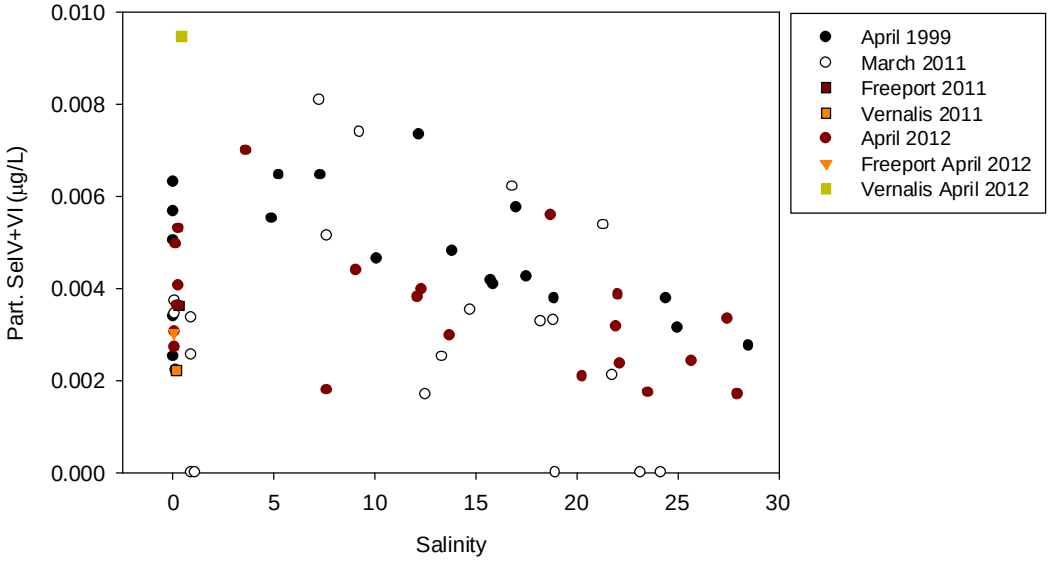

Figure 4-28
Wet weather particulate adsorbed selenite + selenate concentrations sampled in NSFB during April 1999, March 2011 and April 2012. Also shown are data from the riverine sources at Freeport (Sacramento River) and at Vernalis (San Joaquin River).

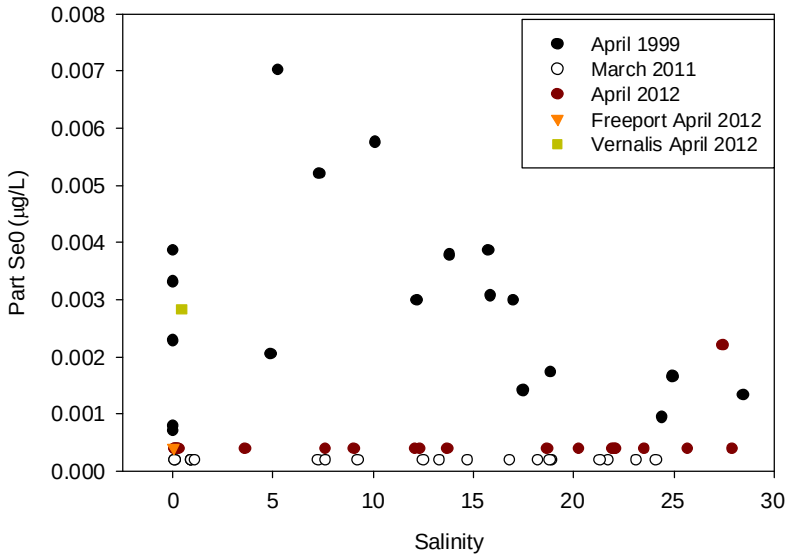

Figure 4-29
Wet weather particulate elemental selenium concentrations in NSFB sampled during April 1999, March 2011 and April 2012. Also shown are data from the riverine sources at Freeport (Sacramento River) and at Vernalis (San Joaquin River).

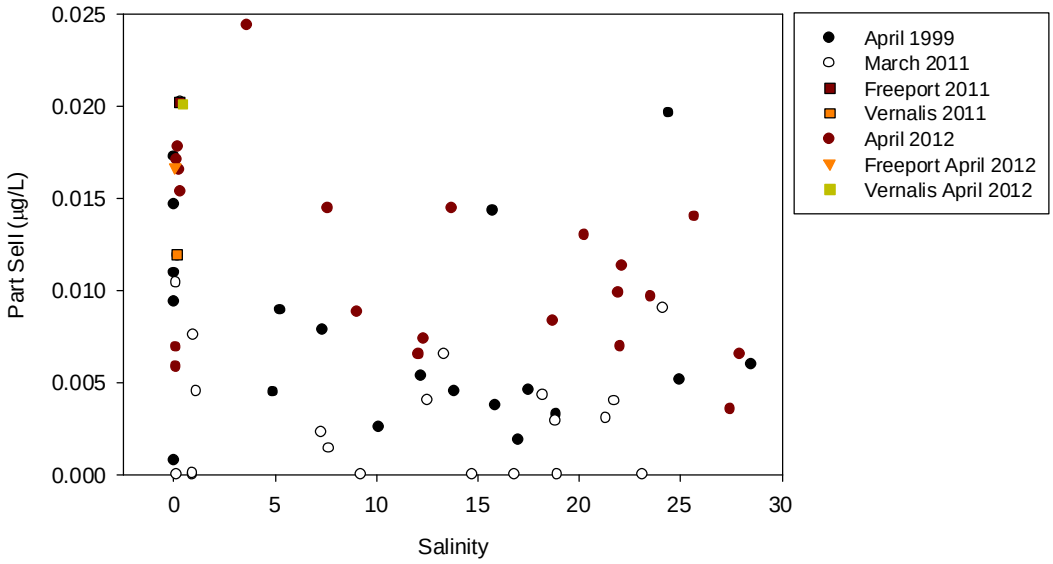

Figure 4-30
Wet weather particulate organic selenium concentrations in NSFB sampled during April 1999, March 2011 and April 2012. Also shown are data from the riverine sources at Freeport (Sacramento River) and at Vernalis (San Joaquin River).

4.3 Receiving Water Samples (Dry Weather, 2010–2011)

Plots of receiving water samples are presented and discussed below for each individual refinery. These plots are presented at a different spatial scale, to identify dilution and near-field effects over a distance of meters, compared to the transect sampling, which covered a span of more than a hundred kilometers.

For the purposes of this study, the tidal state, "ebb" is only an approximation and does not indicate zero directional flow but only that the surface flow direction was non-discernible. Sub-surface flows at the diffuser could be moving in an inland or seaward direction. Additionally, the terms, "upstream" and "downstream" are meant to convey directional information related to the diffuser center-line. The "upstream" location is the eastern-most station and the "downstream" location is the western-most station.

Valero

Receiving water samples were collected from the vicinity of the Valero outfall diffuser on September 13, 2010 and October 06, 2011 and analyzed for dissolved and particulate selenium species. Samples were collected during a flood tide for both events.

The pre-sampling reconnaissance to locate Valero's outfall pipe and diffuser using coordinates provided by Valero and the vessel's depth finder was not successful as no apparent bathymetric anomalies could be located. The effort to locate the diffuser included cruising in a grid pattern over the area where the diffuser was reported to be located. The grid extended from near shore to the shipping channel. Once it was determined that the location of the diffuser could not be clearly identified, the study team decided to use the coordinates that were provided to us by Valero staff for the first dry weather event and work with Valero staff to physically locate the point where the

discharge pipe goes underground. This issue was resolved by the next sampling event (wet weather – 2011).

The specific challenges encountered and improvements in our approach in sampling the receiving water off the Valero outfall and diffuser for the September 2010 dry weather event are discussed below.

Discharge Pipe Location – The location of the discharge pipe as it leaves land and enters the estuary is obscured by the presence of dense reeds so no visual confirmation of the pipe location was possible. Using the coordinates of the outfall that were provided by the refinery provided sample locations that were upstream of the assumed location of the outfall (Figure 2-2), with sample ID "Val-01" being closest to the outfall and "Val-02" and "Val-03" being further upstream. This issue was resolved during the next sampling event (wet weather – 2011) when refinery staff physically flagged the point where the discharge pipe goes underground.

Dissolved Fraction – The September 2010 dissolved total selenium concentrations were greatest at the 20m upstream sites (Val-02 and Val-03), with concentrations being 0.23 µg/L and 0.20 µg/L, respectively. Selenium concentrations were lowest (0.11 µg/L) at the downstream site (Val-01). The October 2011 data indicate no such pattern, with all concentrations being an order of magnitude less than observed during the previous dry weather event and ranging from 0.03 to 0.04 µg/L (Figure 4-31).

Particulate Fraction – The September 2010 particulate total selenium concentrations were slightly higher at Val-02 (0.014 µg/L) and lower at Val-01 and Val-03, with particulate total selenium concentrations being 0.012 µg/L and 0.009 µg/L, respectively. The October 2011 data indicate that particulate selenium concentrations were 2–3 times greater than those observed in the previous dry weather event and greatest at the upstream site "Val-03", with the range being 0.034 to 0.046 µg/L (Figure 4-32). This could be caused by the significantly lower TSM concentrations measured during the September 2010 event (23–36 mg/L) versus those reported for the October 2011 event (123–191 mg/L) (Tables B-4a and B-4b)

Tesoro

Receiving water samples were collected from the end of the Tesoro refinery pier on September 9, 2010 and October 6, 2011 and analyzed for dissolved and particulate selenium species.

The September 9, 2010 receiving water samples from the Tesoro refinery were collected from a location at the end of their pier (Figure 2-4). The vessel was positioned as close to the diffuser at the end of the pier as safely as possible and the sample collected. However, a combination of strong winds, ebb tide currents and no safe area to secure the vessel made it impossible to collect the up current sample. The decision was made by the vessel captain, project safety officer, Regional Board staff and Dr. Greg Cutter that the up current sample would be abandoned and that we would collect one sample from the discharge point (Tes-03) and two down current samples (Tes-01 and Tes-02). These samples were collected as close to 10m down current of the diffuser center-line (Tes-03) as was safely possible due to the presence of a number of metal cross-beam bolts protruding from the pier and the strong winds that were pushing the vessel against them. Future sampling efforts at this refinery were scheduled around absolute slack tide at this location so that both up and down current samples can be safely collected. The 2011 dry weather samples were collected during a slack tide.

Dissolved Fraction – The September 2010 dissolved total selenium concentrations were higher at the diffuser centerline (0.18 µg/L) and slightly lower at the downstream samples (0.14 and 0.15 µg/L) The October 2011 data indicated that the total selenium concentrations were approximately

2.5 times greater at the upstream location (Tes-03) (0.027 µg/L) than they were at either of the diffuser center-line (Tes-02) or downstream (Tes-01) stations (Figure 4-33).

Particulate Fraction – The September 2010 particulate total selenium concentrations followed the pattern observed for the dissolved total selenium concentrations, with the greatest concentrations observed in samples collected from the diffuser center-line (0.045 µg/L) and lower at the two downstream samples (0.02 µg/L). The October 2011 data indicated that the total selenium concentrations were approximately equal at all three stations; ranging from 0.016 – 0.022 µg/L and mirrored closely the values observed for "Tes-01" and "Tes-02" during the September 2010 event (Figure 4-34).

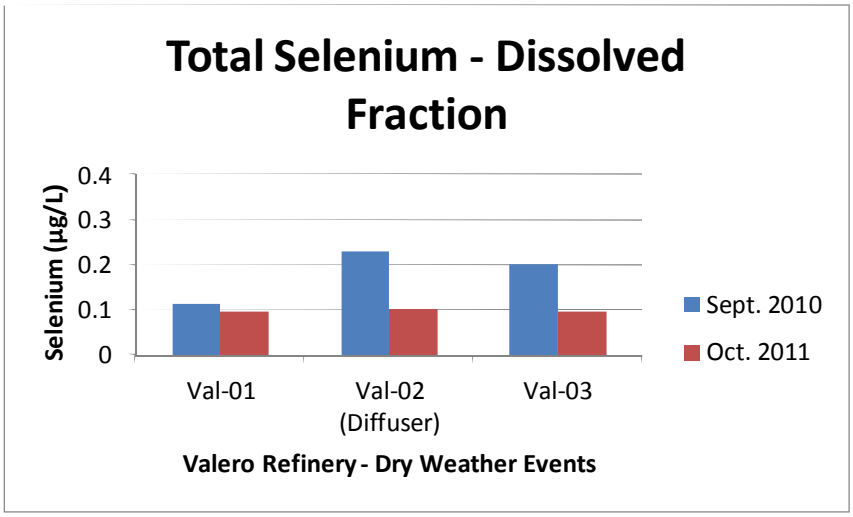

Figure 4-31
Dry weather: Dissolved total selenium concentrations at the Valero Refinery outfall in the vicinity of the diffuser center-line. It should be noted that, for the September 2010 sample, "Val-01" was closer to the diffuser outfall than was "Val-02".

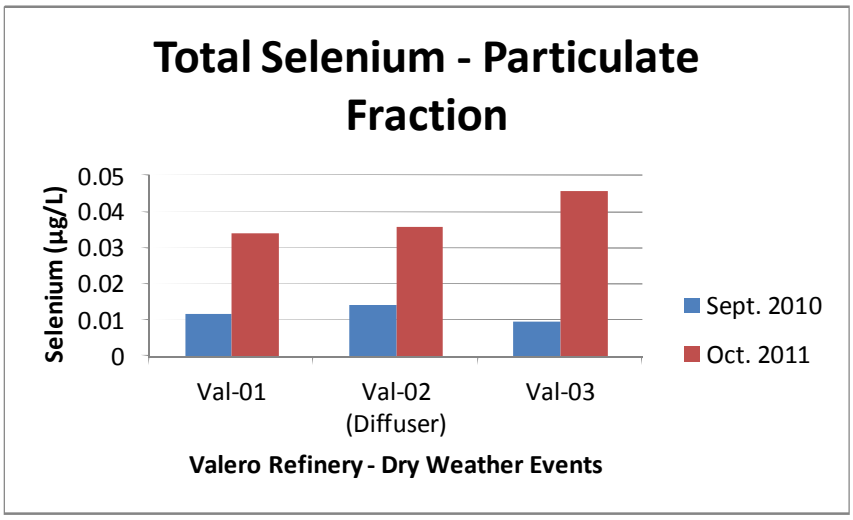

Figure 4-32
Dry weather: Particulate total selenium concentrations at the Valero Refinery outfall in the vicinity of the diffuser center-line. It should be noted that, for the September 2010 sample, "Val-01" was closer to the diffuser outfall than was "Val-02". *Note that the particulate concentrations and y-axis scale are an order of magnitude smaller than for dissolved concentrations.*

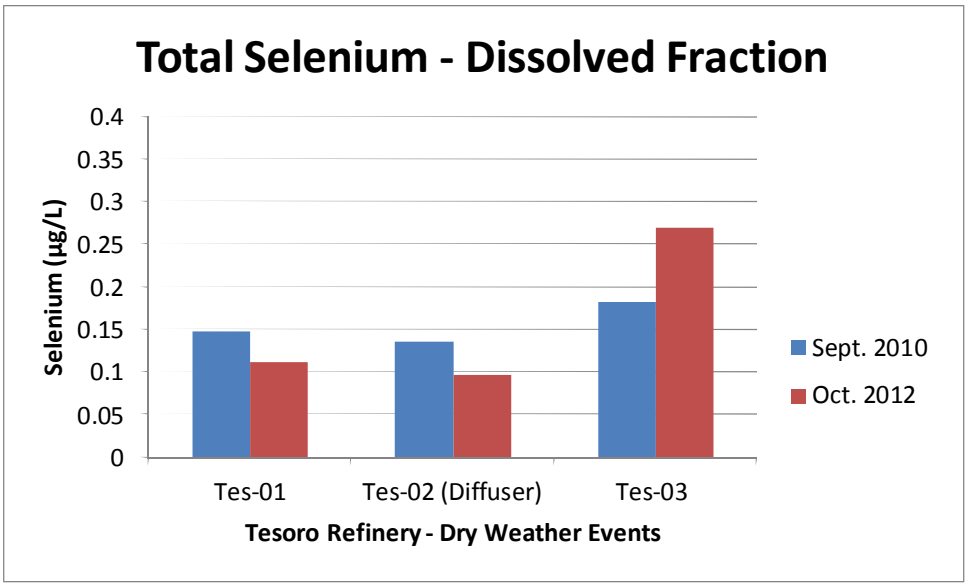

Figure 4-33
Dry weather: Dissolved total selenium concentrations at the Tesoro diffuser center-line (Tes-03) and downstream sites (Tes-01 and Tes-02) for the September 2010 event and diffuser center-line (Tes-02) and upstream (Tes-03) and downstream (Tes-01) sites during the October 2011 event.

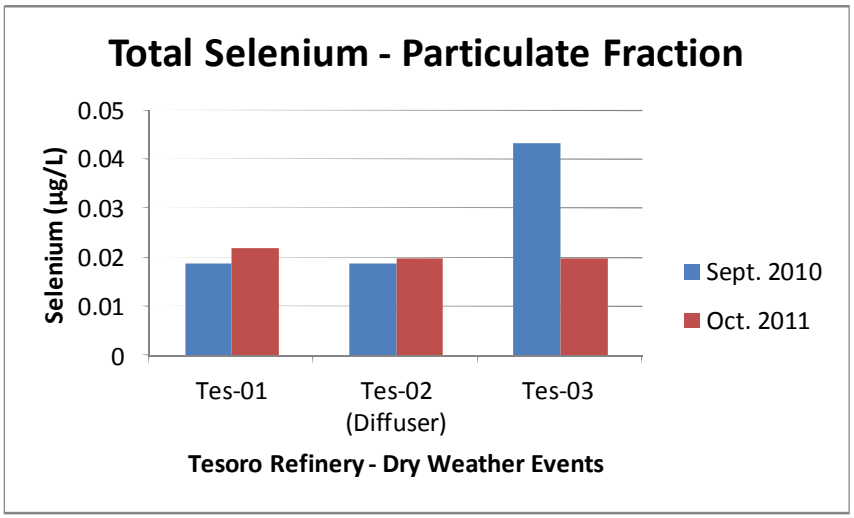

Figure 4-34
Dry weather: Particulate total selenium concentrations at the Tesoro diffuser center-line (Tes-03) and downstream sites (Tes-01 and Tes-02) for the September 2010 event and diffuser center-line (Tes-02) and upstream (Tes-03) and downstream (Tes-01) sites during the October 2011 event. *Note that the particulate concentrations and y-axis scale are an order of magnitude smaller than for dissolved concentrations.*

Shell

Receiving water samples were collected from under the Shell refinery pier on September 9, 2010 and adjacent to the pier on October 5, 2011 and analyzed for dissolved and particulate selenium species. The September 2010 samples were collected from below the wharf because a ship was in port. Samples were collected during an ebb tide during the 2010 event and a slack tide during the 2011 event.

Dissolved Fraction – The September 2010 dissolved total selenium concentrations were highest at the downstream (Shell-01) site (0.35 µg/L) and approximately the same at the diffuser center-line (Shell-02) and upstream (Shell-03) sites (0.18 µg/L and 0.2 µg/L, respectively). No such pattern was observed for the October 2011 dissolved total selenium concentrations which were very similar between the diffuser (Shell-02), upstream (Shell-03) and downstream (Shell-01) stations and ranged from 0.10 to 0.14 µg/L (Figure 4-35).

Particulate Fraction – The September 2010 particulate total selenium concentrations followed the pattern observed for the dissolved total selenium concentrations, with the greatest concentrations observed at the downstream site (0.016 µg/L) and lower at the diffuser center-line and upstream sites (0.004 µg/L and 0.008 µg/L, respectively). The October 2011 data follow a similar pattern to those observed in September 2010; lower at the diffuser (0.01 µg/L) and higher at the upstream (eastern-most) (0.016 µg/L) and downstream (western-most)(0.014 µg/L) sites (Figure 4-36).

Phillips 66

Receiving water samples were collected from under the Phillips 66 refinery pier on September 13, 2010 and October 11, 2011and analyzed for dissolved and particulate selenium species. All samples for the two dry weather events were collected during a slack tide.

Dissolved Fraction – The September 2010 dissolved total selenium concentrations were greatest at the diffuser center-line site (0.22 µg/L) and approximately the same at the downstream and upstream sites (0.12 µg/L and 0.11 µg/L, respectively). The diffuser center-line sample for the October 2011 event was broken during transit so there is no value to report. However, the dissolved total selenium concentrations in the upstream (P66-03: 0.10 µg/L) and downstream (P66-01: 0.11 µg/L) samples were very similar to those observed during the September event (Figure 4-37).

Particulate Fraction – The September 2010 particulate total selenium concentrations were lowest at the diffuser center-line (0.003 µg/L) and elevated at the downstream and upstream sites (0.007 µg/L and 0.008 µg/L, respectively), while they were fairly consistent during the October 2011 event, with the concentrations for each of the samples being approximately 0.01 µg/L (Figure 4-38).

Chevron

Receiving water samples were collected from over and near the Chevron diffuser on September 9, 2010 and October 3, 2011and analyzed for dissolved and particulate selenium species. Both sets of samples were collected during an ebb tide.

Dissolved Fraction – The September 2010 dissolved total selenium concentrations were similar across the three sites at this location and varied by approximately 0.06 µg/L. The greatest concentrations were observed at Chev-01 (0.17 µg/L), with slightly lower concentrations being measured over the diffuser center-line (0.15 µg/L) and at Chev-03 (0.11 µg/L). The October 2011 concentrations were also very similar across the three sites and varied by 0.02 µg/L between the site with the lowest concentration (Chev-02: 0.077 µg/L) and the site with the highest concentration (Chev-03: 0.098 µg/L) (Figure 4-39).

Particulate Fraction – The September 2010 particulate total selenium concentrations were greatest at the diffuser center-line (0.014 µg/L) and lower at sites Chev-03 (0.009 µg/L) and Chev-01 (0.005 µg/L). The October 2011 concentrations varied by approximately 0.03 µg/L between the stations with the lowest and highest concentrations and ranged from a low of 0.007

µg/L at the diffuser center-line station and a high of 0.01 µg/L at the downstream station (Chev-03) (Figure 4-40).

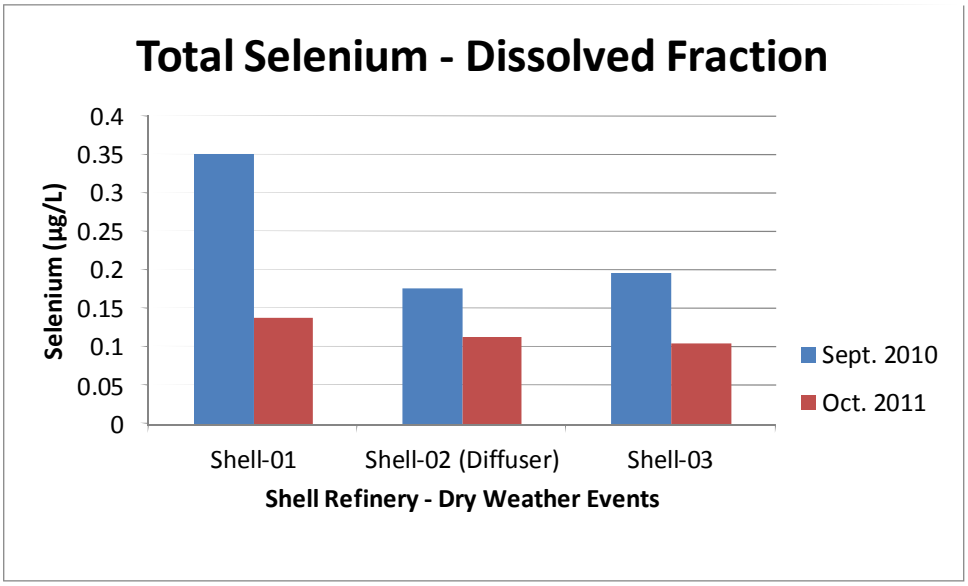

Figure 4-35
Dry weather: Dissolved total selenium concentrations at the Shell diffuser center-line (Shell-02), downstream site (Shell-01) and upstream site (Shell-03).

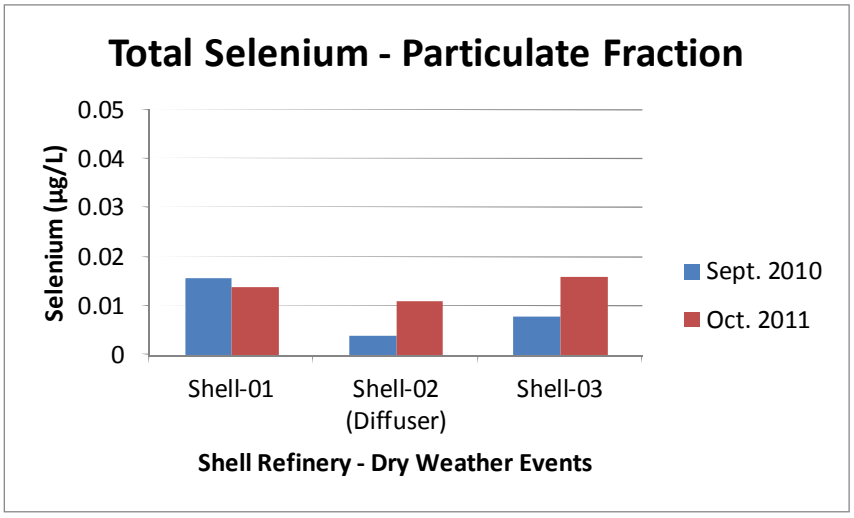

Figure 4-36
Dry weather: Particulate total selenium concentrations at the Shell diffuser center-line (Shell-02); downstream site (Shell-01) and upstream site (Shell-03). *Note that the particulate concentrations and y-axis scale are an order of magnitude smaller than for dissolved concentrations.*

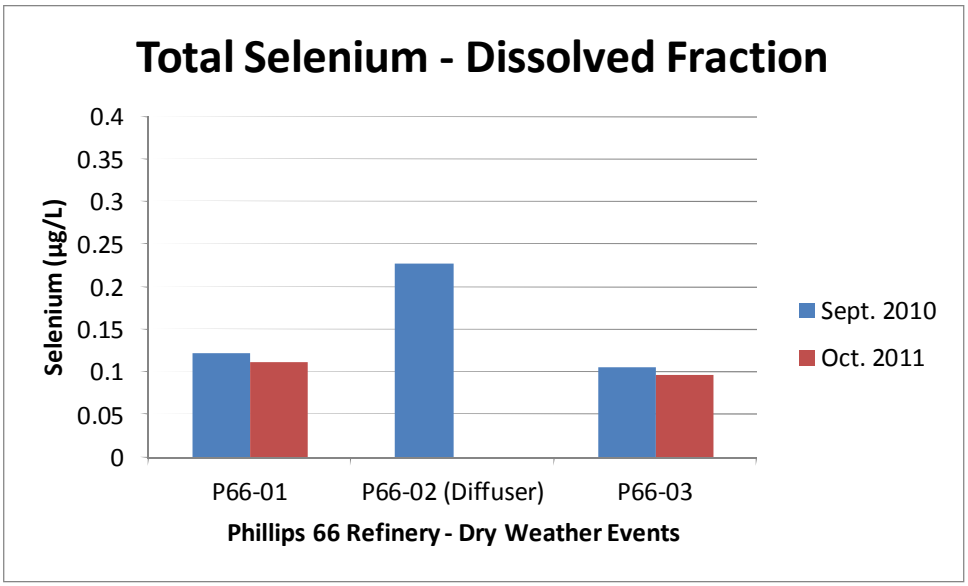

Figure 4-37
Dry weather: Dissolved total selenium concentrations at the Phillips 66 diffuser center-line (P66-02), downstream site (P66-03) and upstream site (P66-01). The P66-02 sample for October 2011 was broken during shipment to the lab.

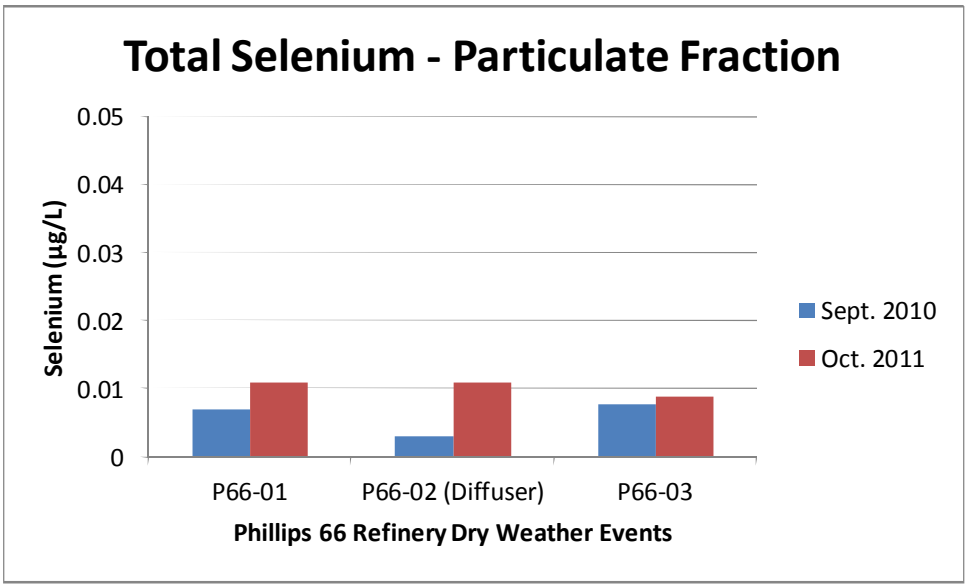

Figure 4-38
Dry weather: Particulate total selenium concentrations at the Phillips 66 diffuser center-line (P66-02); downstream site (P66-03) and upstream site (P66-01). *Note that the particulate concentrations and y-axis scale are an order of magnitude smaller than for dissolved concentrations.*

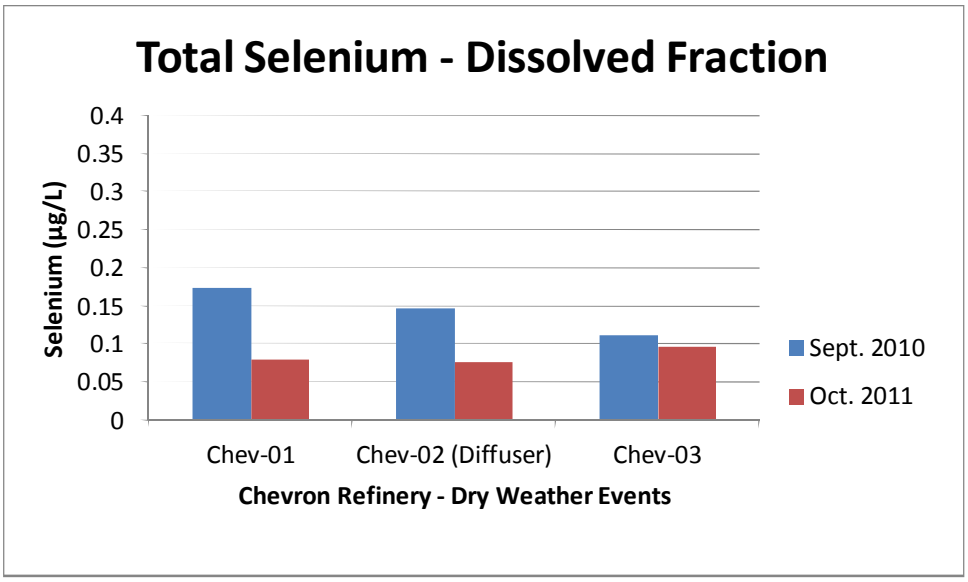

Figure 4-39
Dry weather: Dissolved total selenium concentrations at the Chevron diffuser center-line (Chev-02), downstream (Chev-03) and upstream (Chev-01) sites.

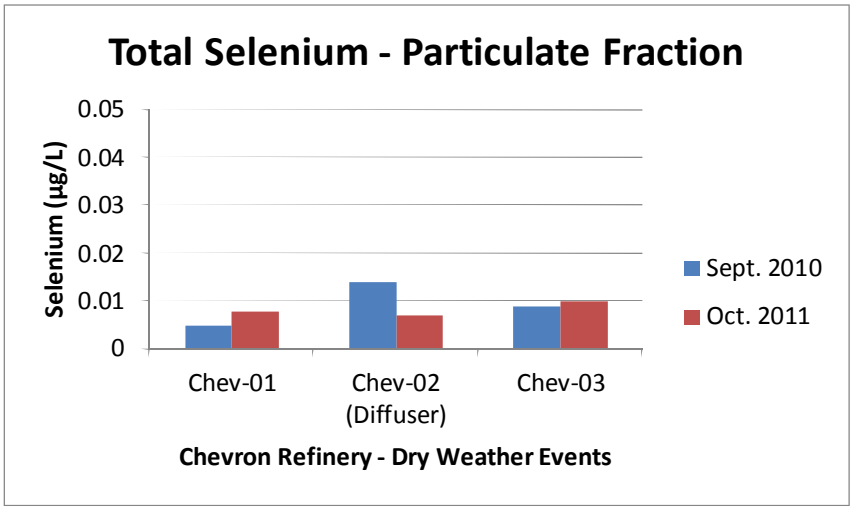

Figure 4-40
Dry weather: Particulate total selenium concentrations at the Chevron diffuser center-line (Chev-02), downstream (Chev-03) and upstream (Chev-01) sites. *Note that the particulate concentrations and y-axis scale are an order of magnitude smaller than for dissolved concentrations.*

Refinery Selenium Speciation

Dissolved selenium sampled in the receiving waters of the refineries showed some variations across refineries, although the concentrations were mostly dominated by selenate (Figure 4-41), representing 60–78% of the total dissolved selenium. Particulate selenium concentrations showed large variations across the sites but were dominated by organic selenide and adsorbed selenite/selenate (Figure 4-42). Elemental selenium was largely at non-detect levels. The lack of elemental selenium in the particulate phase suggests that selenium originating from resuspension of bed sediments was minimal during the sampling.

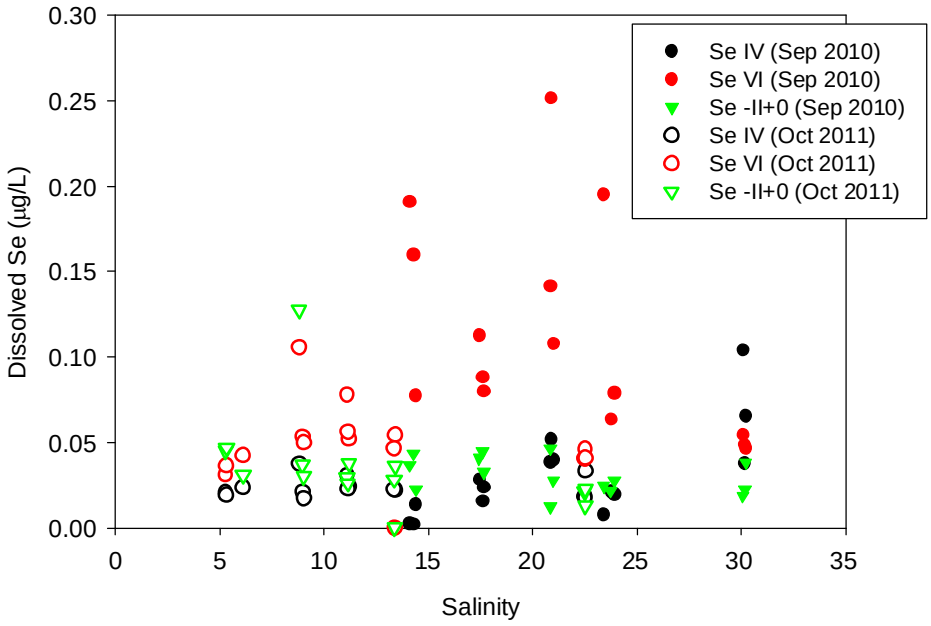

Figure 4-41
Dry weather: Dissolved selenium species in the receiving waters of the five refineries sampled during September 2010 and October 2011.

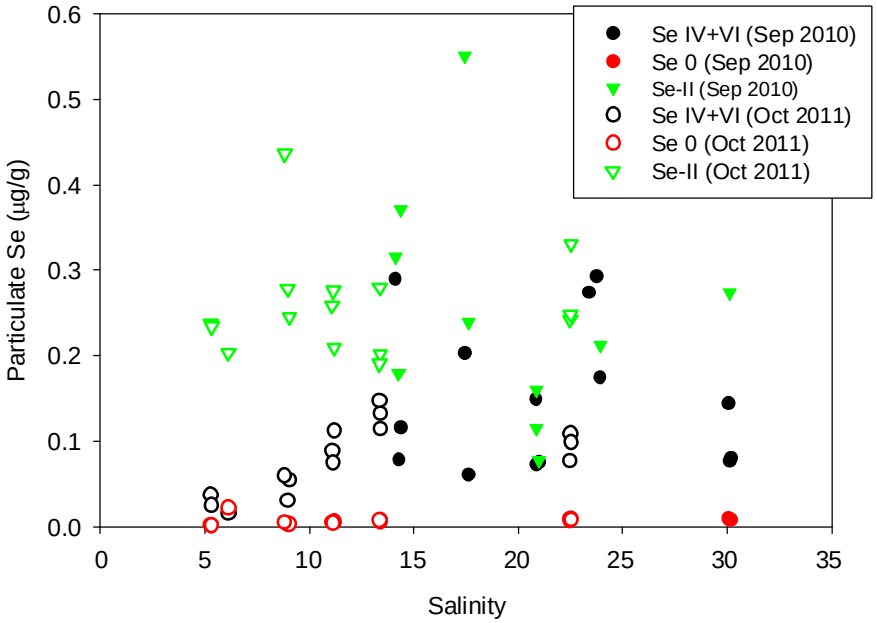

Figure 4-42
Dry weather: Particulate selenium concentrations in the receiving water of the five refineries sampled during September 2010 and October 2011.

Receiving Water Concentrations Compared to Transect Concentrations (Dry Season)

Concentrations of different selenium species through the estuary transect are compared to the refinery receiving water concentrations in Figure 4-43 through Figure 4-50, and discussed individually below. These data are shown for the 2010 and 2011 dry season sampling.

- Selenite data in the dissolved phase are shown along the estuary in Figure 4-43. Concentrations at two refinery locations are in excess of the refinery transect values.
- Selenate data in the dissolved phase are shown in Figure 4-44. For this species, receiving water concentrations exceeded transect concentrations at several locations in the mid-estuary region.
- Selenide concentrations are shown in Figure 4-45 and receiving water concentrations appear to be similar to or lower than the transect concentrations.
- Total selenium concentrations (Figure 4-46) are higher than the estuary concentrations by a factor of two or more at several outfall locations.
- Particulate concentrations in the receiving water samples, shown in total form and at the species level (Figure 4-47 through Figure 4-50) show elevated levels of selenide at some locations, but not for the other species. Total particulate concentrations are exceeded at several locations driven by the selenide contribution.

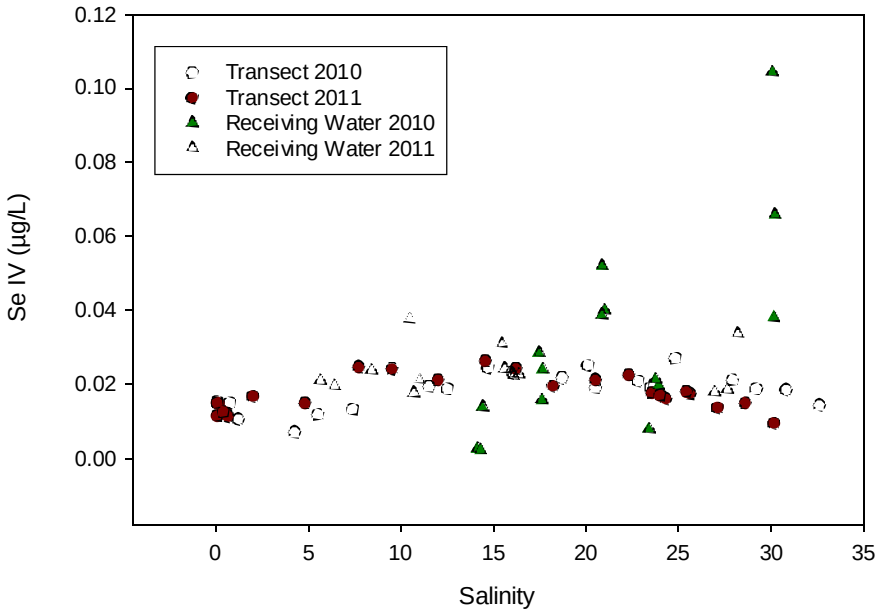

Figure 4-43
Dry weather selenite (SeIV) concentrations across the estuary with data from 2010, 2011 and receiving waters near the five refinery outfalls.

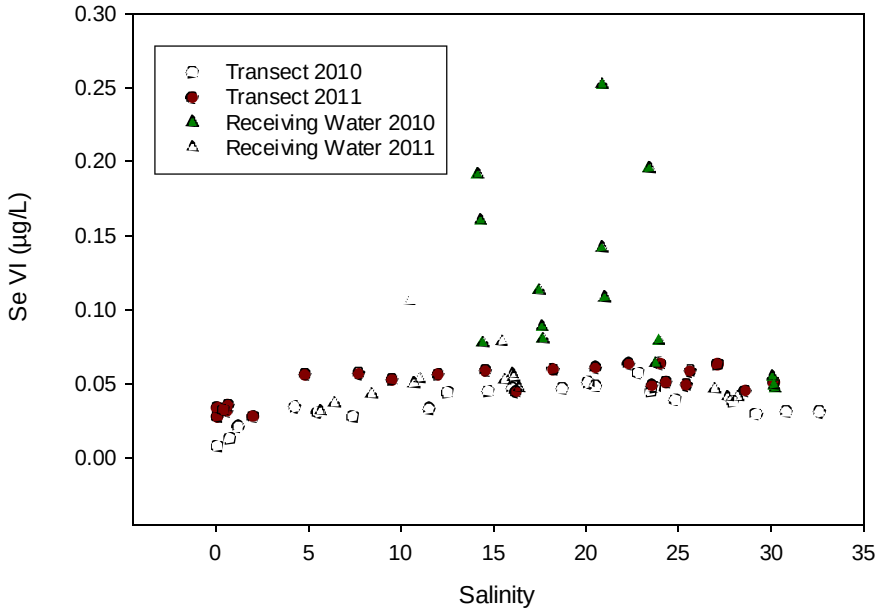

Figure 4-44
Dry weather selenate (SeVI) concentrations across the estuary with data from 2010, 2011 and receiving waters near the five refinery outfalls.

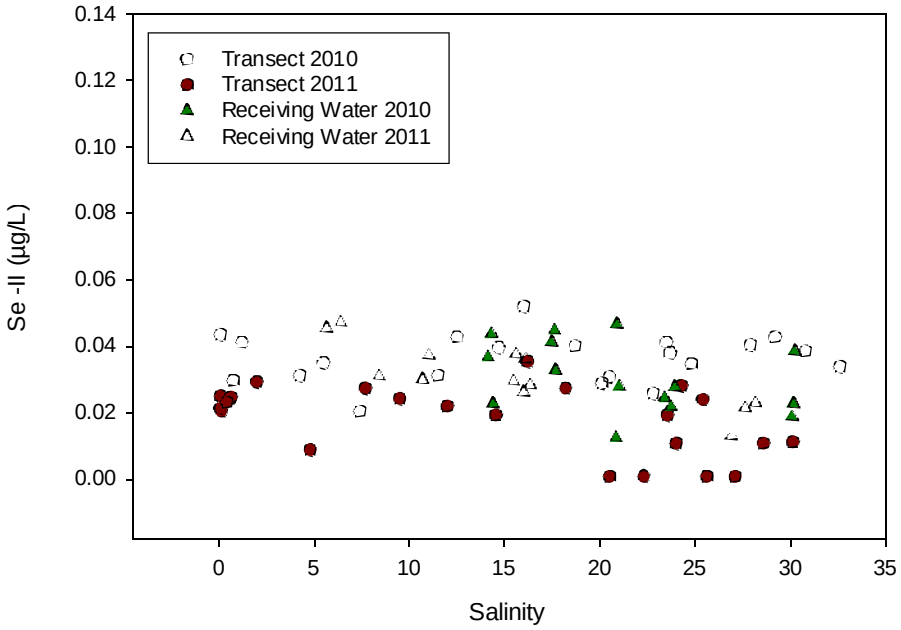

Figure 4-45
Dry weather organic selenium (Se-II) concentrations across the estuary with data from 2010, 2011 and receiving waters near the five refinery outfalls.

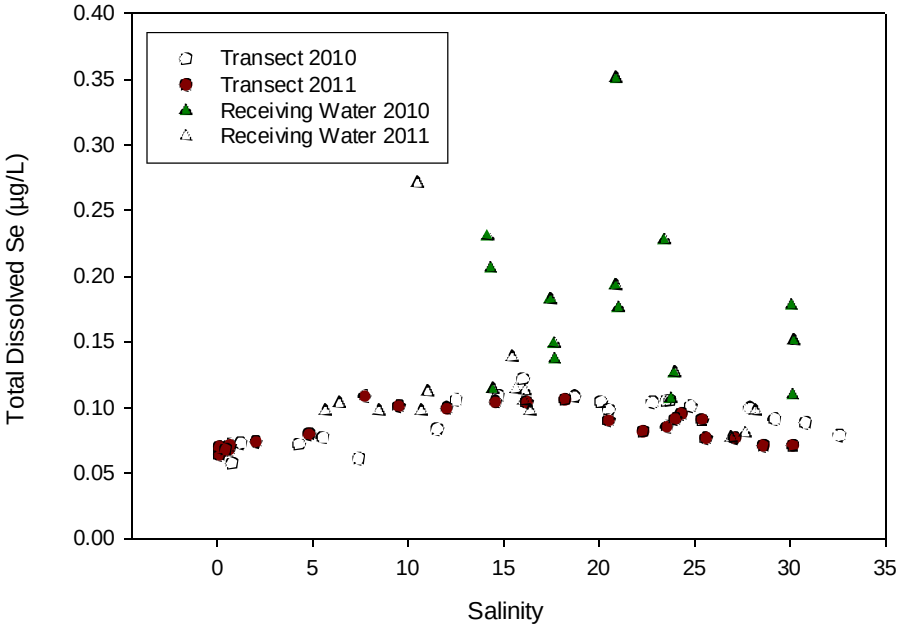

Figure 4-46
Dry weather total dissolved selenium concentrations across the estuary with data from 2010, 2011 and receiving waters near the five refinery outfalls.

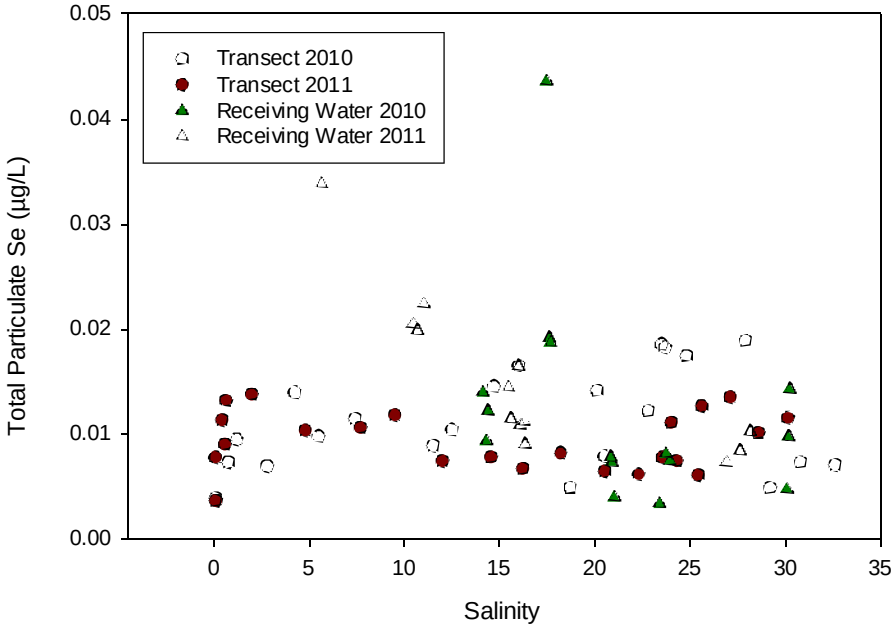

Figure 4-47
Dry weather total particulate selenium concentrations across the estuary with data from 2010, 2011 and receiving waters near the five refinery outfalls.

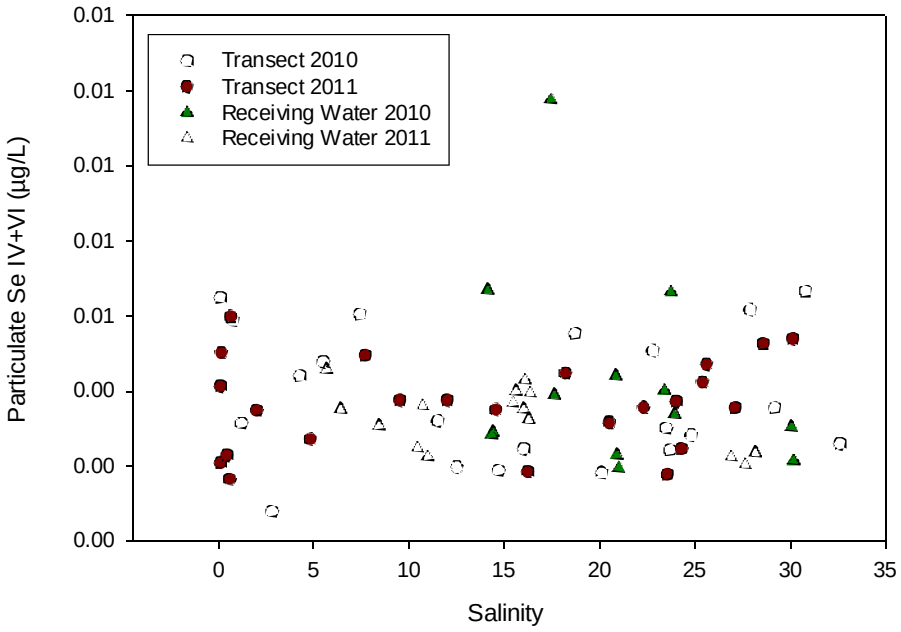

Figure 4-48
Dry weather particulate adsorbed selenite + selenate concentrations across the estuary with data from 2010, 2011 and receiving waters near the five refinery outfalls.

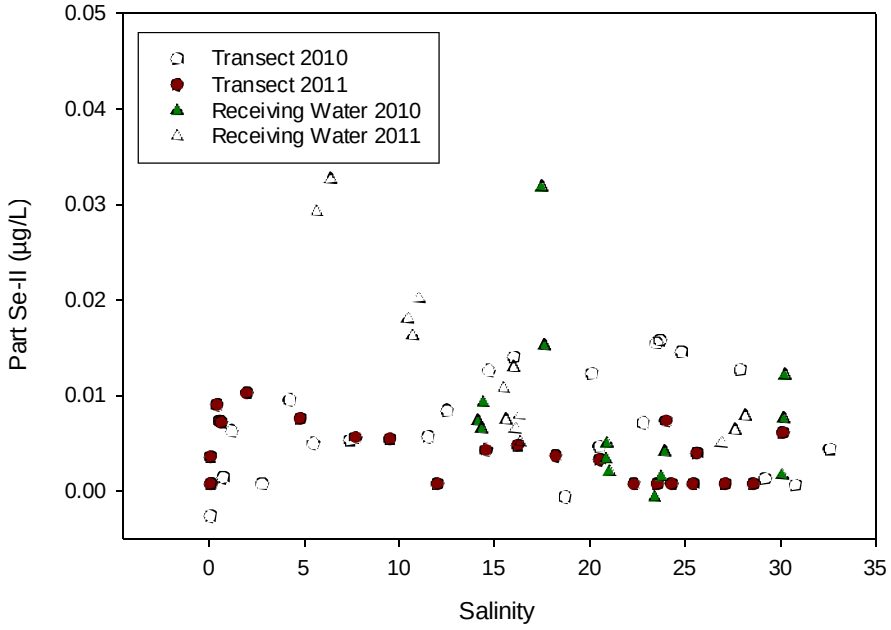

Figure 4-49
Dry weather particulate organic selenium concentrations across the estuary with data from 2010, 2011 and receiving waters near the five refinery outfalls.

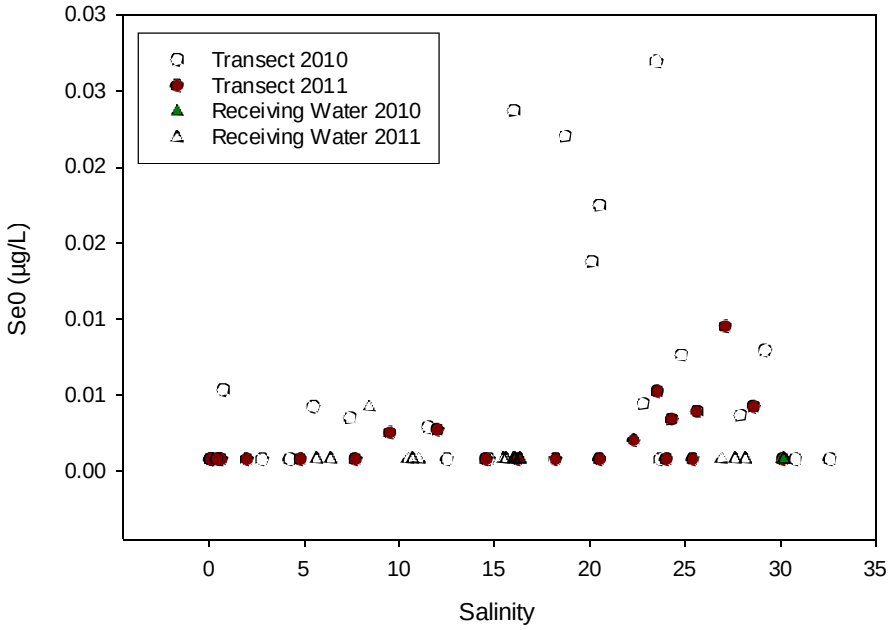

Figure 4-50
Dry weather particulate adsorbed selenite + selenate concentrations across the estuary with data from 2010, 2011 and receiving waters near the five refinery outfalls.

4.4 Receiving Water Samples (Wet Weather, 2011–2012)

The following section presents wet weather sampling near refinery outfalls, using similar approaches used in the prior section for dry weather sampling.

For the purposes of this study, the tidal state, "ebb" is only an approximation and does not indicate zero directional flow but only that the surface flow direction was non-discernible. Sub-surface flows at the diffuser could be moving in an inland or seaward direction. Additionally, the terms, "upstream" and "downstream" are meant to convey directional information related to the diffuser center-line. The "upstream" location is the eastern-most station and the "downstream" location is the western-most station.

Valero

Receiving water samples were collected from the vicinity of the Valero discharge on March 16, 2011and April 11, 2012 and analyzed for dissolved and particulate selenium species. Samples from the 2011 and 2012 events were collected during flood and ebb tides, respectively.

Dissolved Fraction – The March 2011 dissolved total selenium concentrations were the same at the 20m upstream sites (Val-02 and Val-03), with both stations having concentrations of 0.11 µg/L. Selenium concentrations were highest (0.12 µg/L) at the upstream site (Val-01). The same pattern and concentration ranges are observed for the April 2012 results, with the upstream site having a concentration of 0.122 µg/L and the diffuser center-line and downstream sites having concentrations of 0.11 µg/L (Figure 4-51).

Particulate Fraction – The March 2011 particulate total selenium concentrations were greatest at Val-01 (0.007µg/L) and lower at Val-02 and Val-03, with particulate total selenium concentrations being 0.005 µg/L and 0.003 µg/L, respectively, with the April 2011 concentrations exhibiting a similar pattern, albeit with higher concentrations of total selenium. The greatest particulate selenium concentrations were observed at Val-01 (0.027 µg/L), with Val-03 having the lowest concentration (0.015 µg/L) (Figure 4-52).

Tesoro

Receiving water samples were collected from the end of the Tesoro refinery pier on March 22, 2011 and April 25, 2012 and analyzed for dissolved and particulate selenium species. Samples were collected during a weak ebb tide during the 2011 and 2012 sample events.

Dissolved Fraction – The March 2011 dissolved total selenium concentrations were approximately 0.1 µg/L near the diffuser centerline (TES-03) and 10m downstream of the diffuser (TES-02), and were almost twice as high at the station 20m (TES-01) downstream (0.19 µg/L). The April 2012 data indicate that the concentrations of total selenium were approximately equal at all three stations and varied by approximately 0.01 µg/L between the two stations having the lowest concentrations (TES-01 and TES-03) and the diffuser center-line station (TES-02) which had a concentration of 0.09 µg/L (Figure 4-53).

Particulate Fraction – The March 2011 particulate total selenium concentrations followed the pattern observed for the dissolved total selenium concentrations, with the lowest concentrations observed in samples collected from the diffuser center-line (0.010 µg/L) and higher at the two downstream samples (0.012 and 0.023 µg/L). The April 2012 particulate selenium concentration at TES-01was identical to that observed during the March event (0.023 µg/L), however the particulate selenium concentrations at the diffuser center-line (TES-02) and TES-03 (10m downstream from TES-02) exhibited higher concentrations at 0.026 and 0.035 µg/L, respectively

(Figure 4-54). It should be noted that the TSM concentrations at TES-02 and TES-03 were substantially less at these stations during the March 2011 event than they were during the April 2012 event (Tables B-9a and B-9b).

Shell

Receiving water samples were collected from adjacent to the Shell refinery pier on March 16, 2011 and April 12, 2012 and analyzed for dissolved and particulate selenium species. All samples were collected at ebb tide.

Dissolved Fraction – The March 2011 dissolved total selenium concentrations were greatest at the diffuser center-line site (0.81 µg/L) and approximately the same at downstream and upstream sites (0.13 µg/L and 0.39 µg/L, respectively). The April 2012 dissolved selenium concentrations were similar at all three stations and ranged from 0.14 µg/L at Shell-02 (diffuser center-line) to 0.15 µg/L at both Shell-01 and Shell-03 (Figure 4-55).

Particulate Fraction – The March 2011 particulate total selenium concentrations showed the greatest concentrations at the downstream site (0.025 µg/L) and slightly lower at the diffuser center-line and upstream sites (0.024 µg/L and 0.019 µg/L, respectively). The April 2012 particulate selenium concentrations were greatest at the upstream site (0.035 µg/L) and lowest at the downstream site (0.024 µg/L) (Figure 4-56).

Phillips 66

Receiving water samples were collected from under the Phillips 66 refinery pier on March 17, 2011 and April 13, 2012 and analyzed for dissolved and particulate selenium species. All samples were collected during an ebb tide.

Dissolved Fraction – The March 2011 dissolved total selenium concentrations were greatest at the diffuser center-line site (0.35 µg/L) and approximately the same at the downstream and upstream sites (0.12 µg/L and 0.13 µg/L, respectively). The same pattern and magnitude of selenium concentrations was observed during the April 2012 event, with the greatest concentrations being observed at the diffuser center-line site (0.37 µg/L) and approximately the same at the downstream and upstream sites (0.17 µg/L and 0.12 µg/L, respectively) (Figure 4-57).

Particulate Fraction – The March 2011 particulate total selenium concentrations were lower at the diffuser center-line (0.01 µg/L) and elevated at the downstream and upstream sites (0.008 µg/L and 0.011 µg/L, respectively). The particulate selenium concentrations during the April 2012 event varied by slightly more than 0.01 µg/L between the site having the lowest concentration (0.009 µg/L) at P66-02 (diffuser center-line) and that having the greatest concentration of 0.02 µg/L at P66-03 (upstream site) (Figure 4-58).

Chevron

Receiving water samples were collected from over and near the Chevron diffuser on March 16, 2011 and April 10, 2012 and analyzed for dissolved and particulate selenium species. Samples were collected during a slack tide in March and a flood tide in April.

Dissolved Fraction – The March 2011 dissolved total selenium concentrations were similar between the three sites at this location, varying by approximately 0.03 µg/L. The greatest concentrations were observed at Chev-01 (0.11 µg/L), with slightly lower concentrations being measured over the diffuser center-line (0.09 µg/L) and at Chev-03 (0.08 µg/L). A very similar

pattern was observed during the April 2012 event with the dissolved selenium concentrations at all three stations being approximately 0.10 µg/L (Figure 4-59).

Particulate Fraction – The March 2011 particulate total selenium concentrations were lowest at the downstream site Chev-03 (ND) and diffuser center-line (Chev-02) (0.001 µg/L) and highest at the upstream site: Chev-01 (0.017 µg/L). The April 2012 particulate selenium concentrations were very similar at each of the three sites, varying by 0.004 µg/L and ranging from a low of 0.021 µg/L at Chev-03 and 0.025 µg/L at Chev-01 and Chev-02 (Figure 4-60).

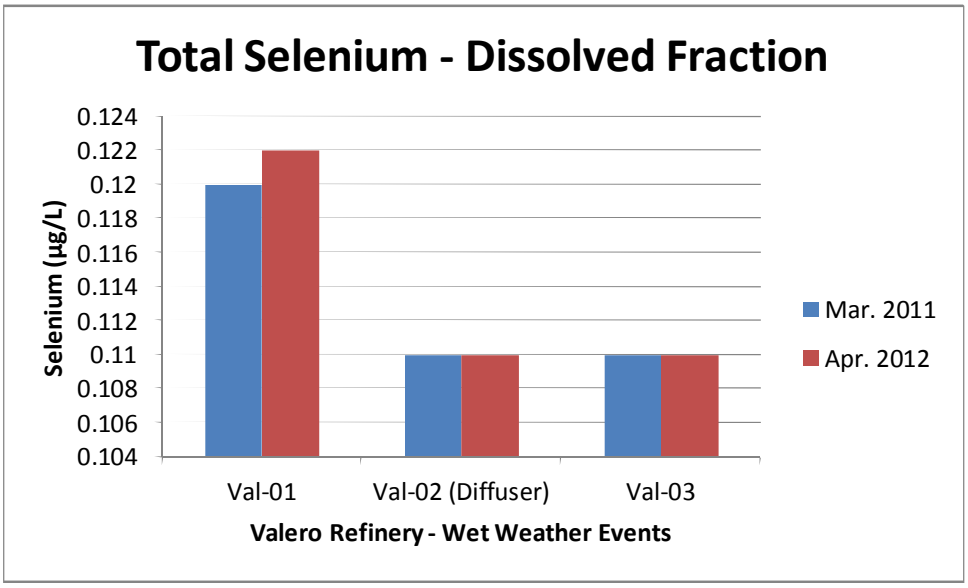

Figure 4-51
Wet weather: Dissolved total selenium concentrations at the Valero Refinery outfall center-line (Val-02) and 10m upstream (Val-03) and 10m downstream (Val-01) sites.

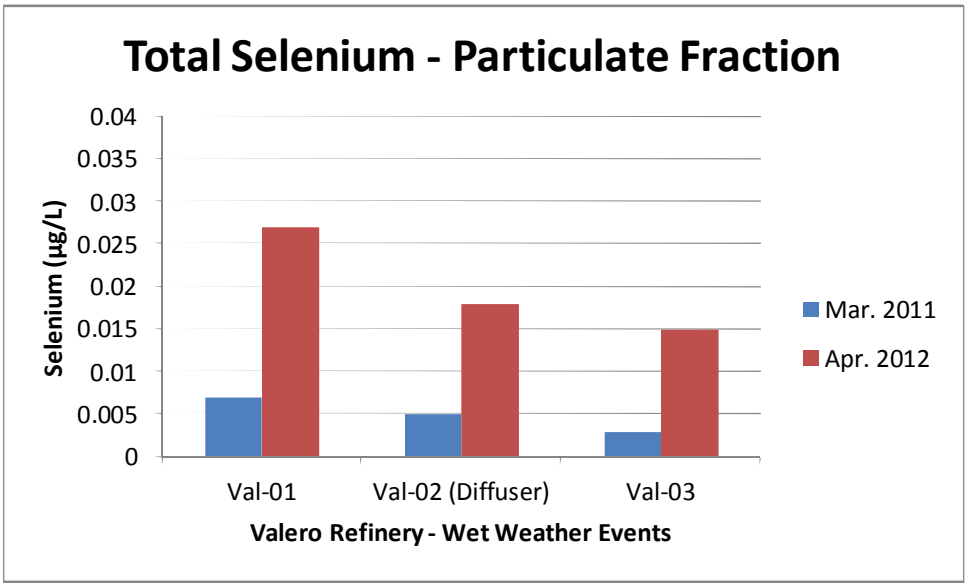

Figure 4-52
Wet weather: Particulate total selenium concentrations at the Valero Refinery outfall center-line (Val-02) and 10m upstream (Val-03) and 10m downstream (Val-01) sites. ***Note that the particulate concentrations and y-axis scale are an order of magnitude smaller than for dissolved concentrations.***

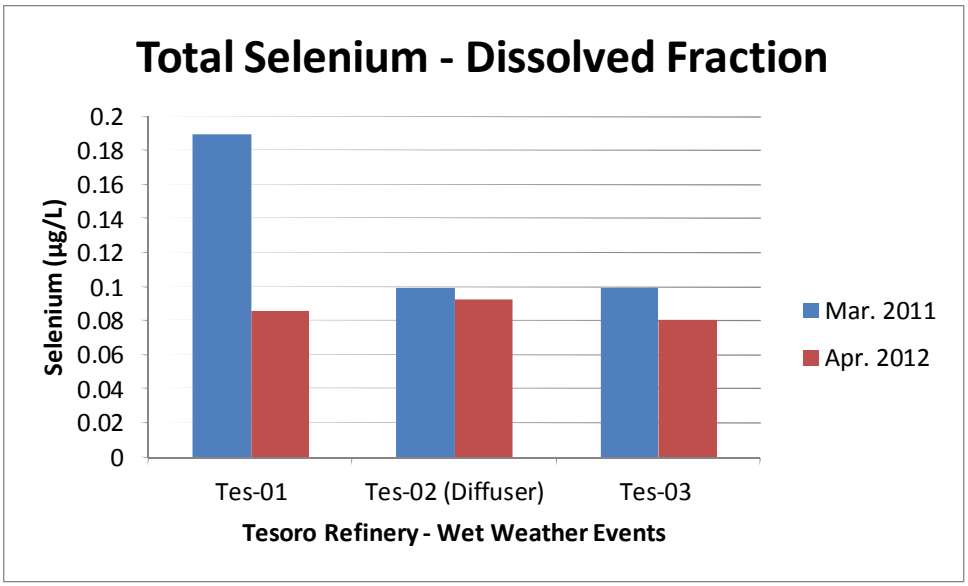

Figure 4-53
Wet weather: Dissolved total selenium concentrations at the Tesoro diffuser center-line (Tes-02) and 10m upstream (Tes-03) and 10m downstream (Tesl-01) sites.

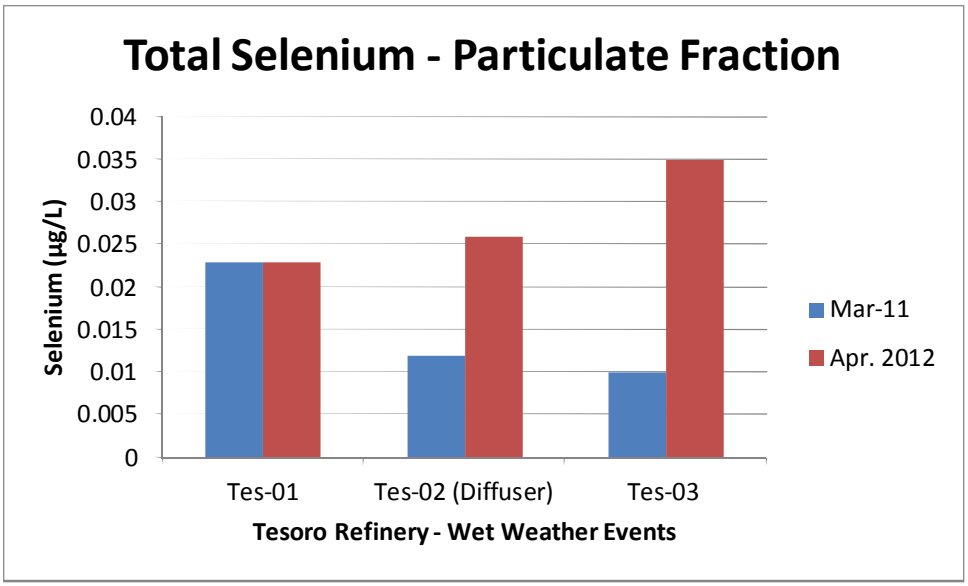

Figure 4-54
Wet weather: Particulate total selenium concentrations at the Tesoro diffuser center-line (Tes-02) and 10m upstream (Tes-03) and 10m downstream (Tesl-01) sites. ***Note that the particulate concentrations and y-axis scale are an order of magnitude smaller than for dissolved concentrations.***

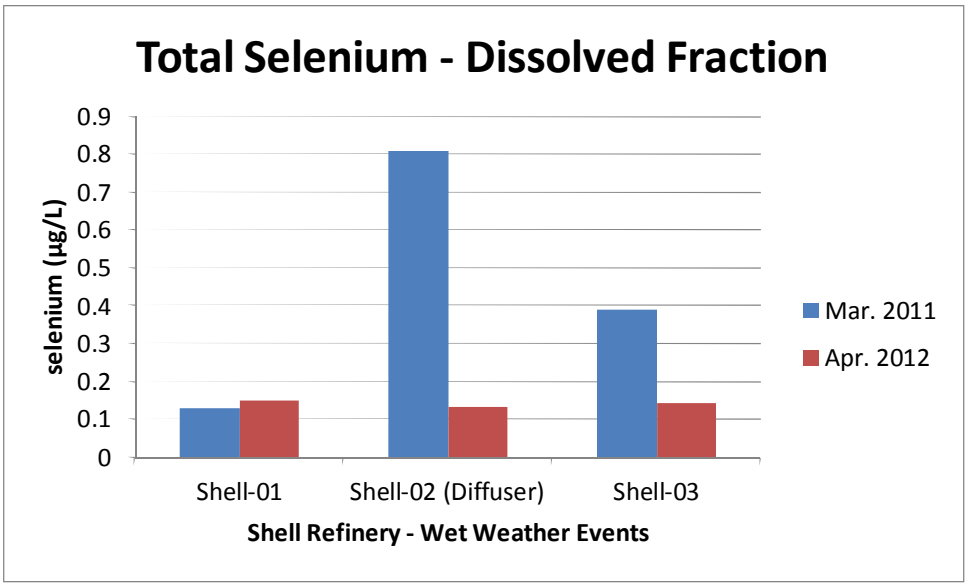

Figure 4-55
Wet weather: Dissolved total selenium concentrations at the Shell refinery diffuser center-line (Shell-02), downstream site (Shell-01) and upstream site (Shell-03).

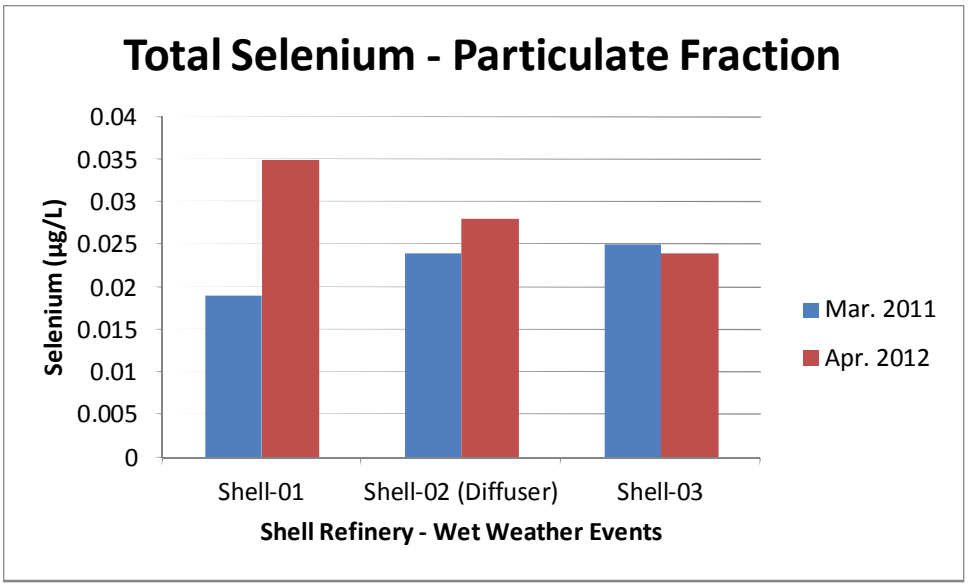

Figure 4-56
Wet weather: Particulate total selenium concentrations at the Shell diffuser center-line (Shell-02); downstream site (Shell-01) and upstream site (Shell-03). *Note that the particulate concentrations and y-axis scale are an order of magnitude smaller than for dissolved concentrations.*

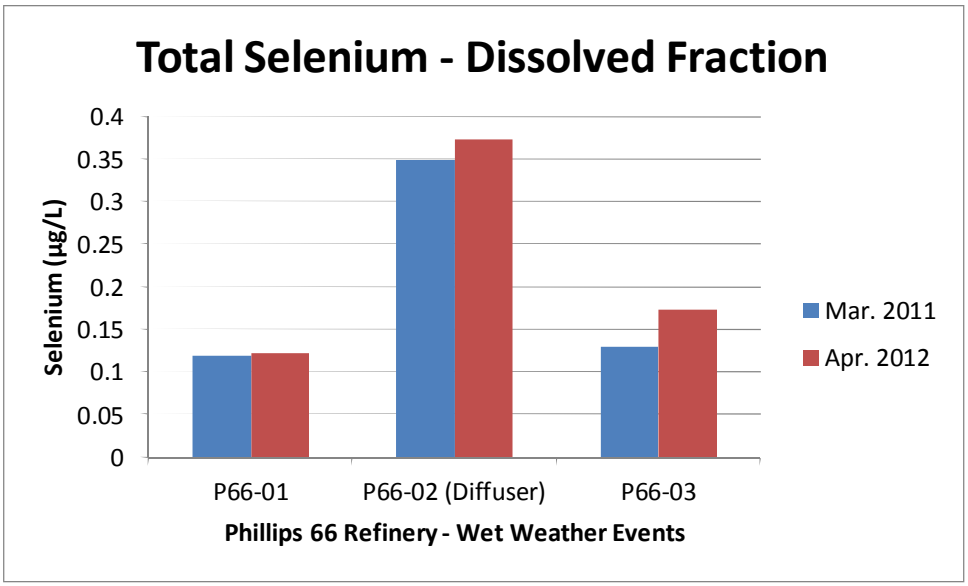

Figure 4-57
Wet weather: Dissolved total selenium concentrations at the Phillips 66 refinery diffuser center-line (P66-02), downstream site (P66-01) and upstream site (P66-03).

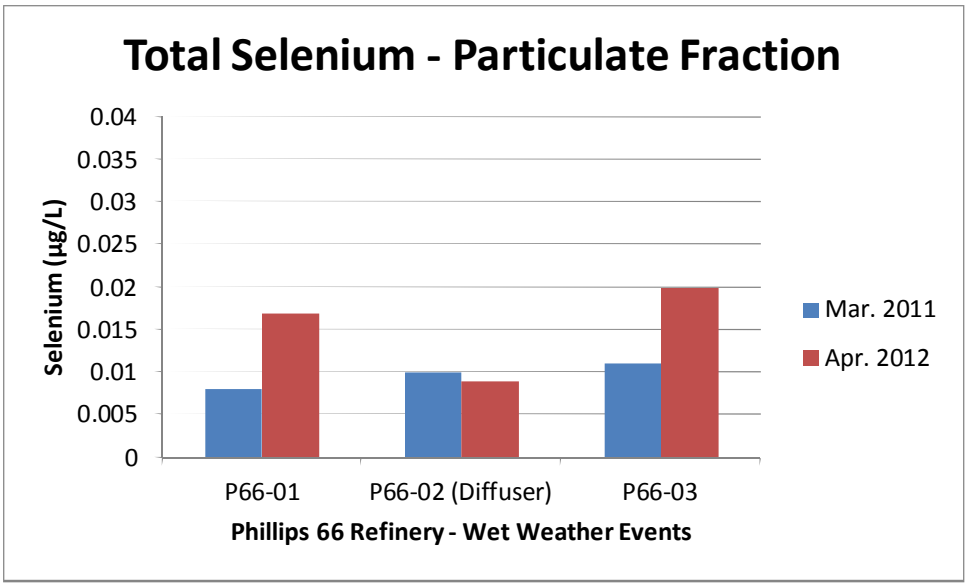

Figure 4-58
Wet weather: Particulate total selenium concentrations at the Phillips 66 diffuser center-line (P66-02); downstream site (P66-01) and upstream site (P66-03). ***Note that the particulate concentrations and y-axis scale are an order of magnitude smaller than for dissolved concentrations.***

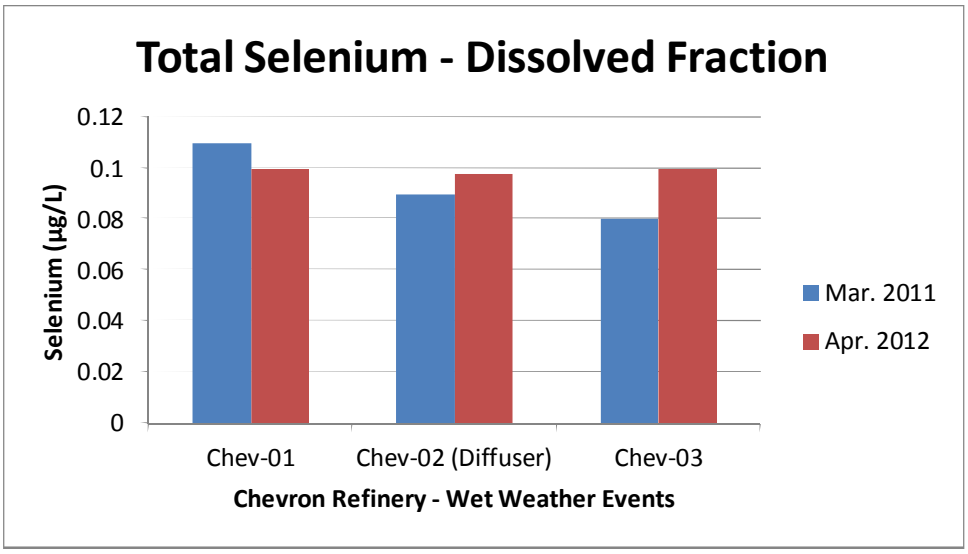

Figure 4-59
Wet weather: Dissolved total selenium concentrations at the Chevron refinery diffuser center-line (Chev-02) and 10m ZID sites (upstream: Chev-01) and (downstream: Chev-03).

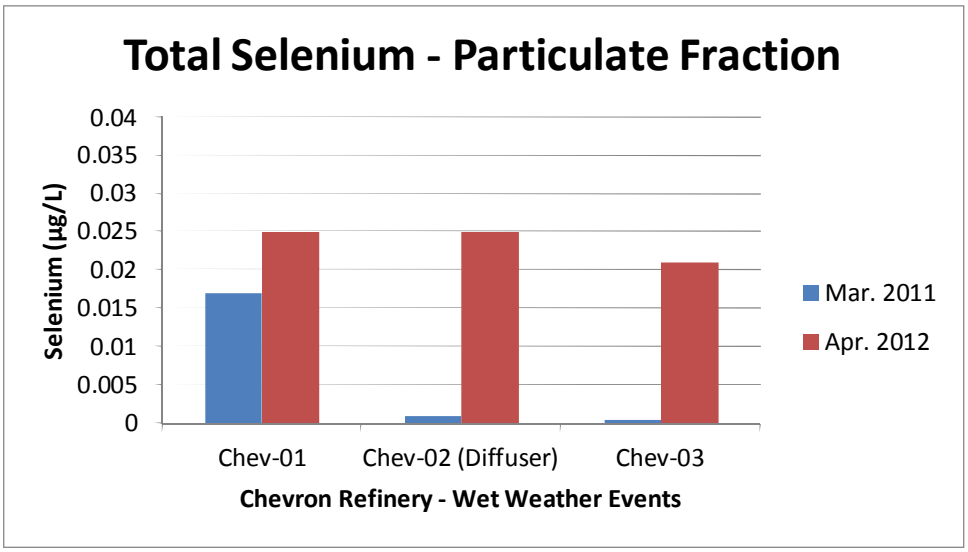

Figure 4-60
Wet weather: Particulate total selenium concentrations at the Chevron refinery diffuser center-line (Chev-02) and 10m ZID sites (upstream: Chev-01) and (downstream: Chev-03). ***Note that the particulate concentrations and y-axis scale are an order of magnitude smaller than for dissolved concentrations.***

Refinery Selenium Speciation

Dissolved selenium sampled in the receiving water near the refinery outfalls showed variations in speciation across sites. Near the refinery outfalls, the speciation was dominated by selenate (Figure 4-61). Selenate comprised 60–78% of the total dissolved selenium in the receiving waters of the most refineries. Selenite and organic selenide were present at similar, and lower, concentrations.

Particulate selenium in receiving waters near refinery outfalls were dominated by adsorbed selenite/selenate and organic selenide (Figure 4-62) and concentrations showed significant variations across the sites.

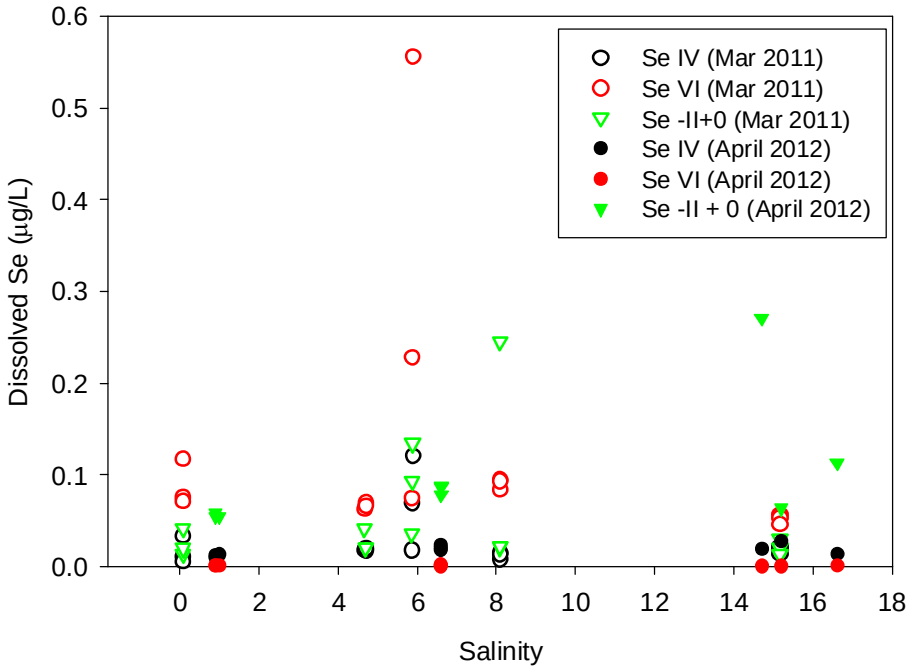

Figure 4-61
Wet weather: Dissolved selenium species in the receiving waters of the five refineries sampled during March 2011 and April 2012.

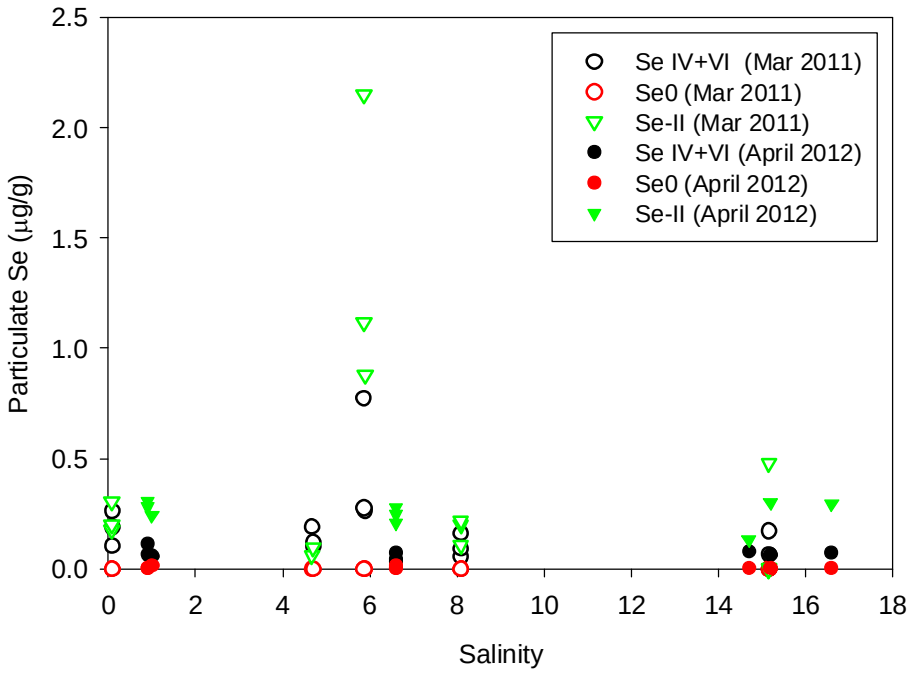

Figure 4-62
Wet weather: Particulate selenium concentrations in the receiving waters of the five refineries sampled during March, 2011 and April 2012.

Receiving Water Concentrations Compared to Transect Concentrations (Wet Season)

Concentrations of different selenium species through the estuary transect are presented in Figure 4-63 through Figure 4-70 and discussed individually below.

- Selenite data in the dissolved phase are shown along the estuary in Figure 4-63. Concentrations near the refinery outfalls are generally similar to estuarine concentrations with two exceptions.
- Selenate data in the dissolved phase are shown in Figure 4-64. Selenium concentrations from the receiving waters of refineries are similar to estuarine values with three samples outside the observed concentration range of the transect samples.
- Selenide (organic selenium, or Se(-II)) concentrations are shown in Figure 4-65. Concentrations from the receiving waters of refinery outfalls are generally lower than the estuarine transect concentrations with four points exceeding the transect values.
- Figure 4-66 shows total dissolved selenium concentrations near each refinery outfall. In most instances these concentrations are similar to estuary concentrations in the vicinity, with higher values at four locations.
- Particulate concentrations in the refinery receiving waters are compared to the estuary transects in Figure 4-67 through Figure 4-70. For total particulate selenium, concentrations are elevated at one location, with all others at the same levels as the estuarine transect. This pattern is also observed for the particulate organic selenium (Figure 4-69) but not for the other species.

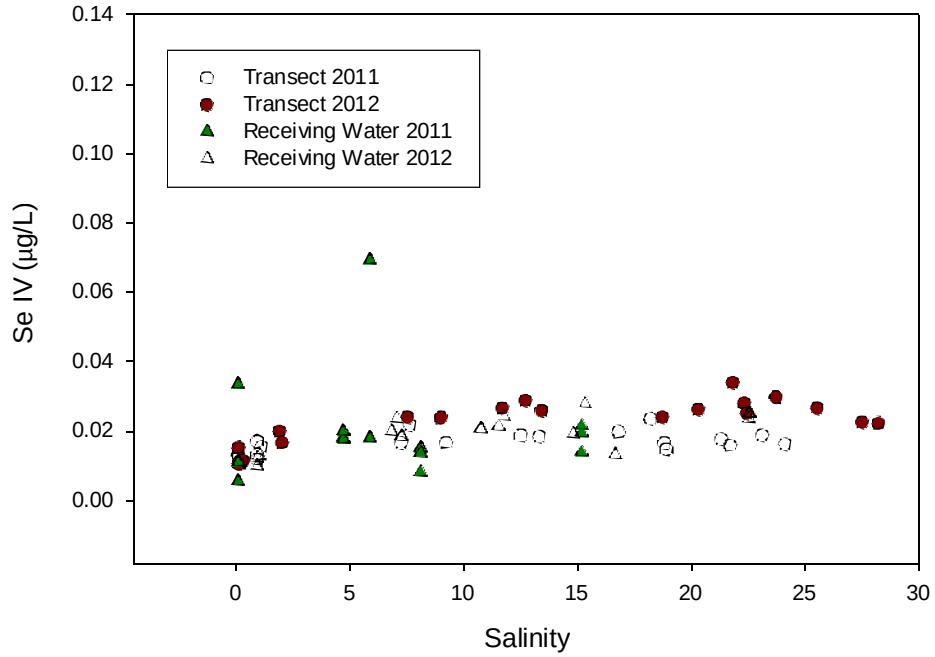

Figure 4-63
Wet weather selenite (SeIV) concentrations across the estuary with data from 2011, 2012 and receiving waters near the five refinery outfalls.

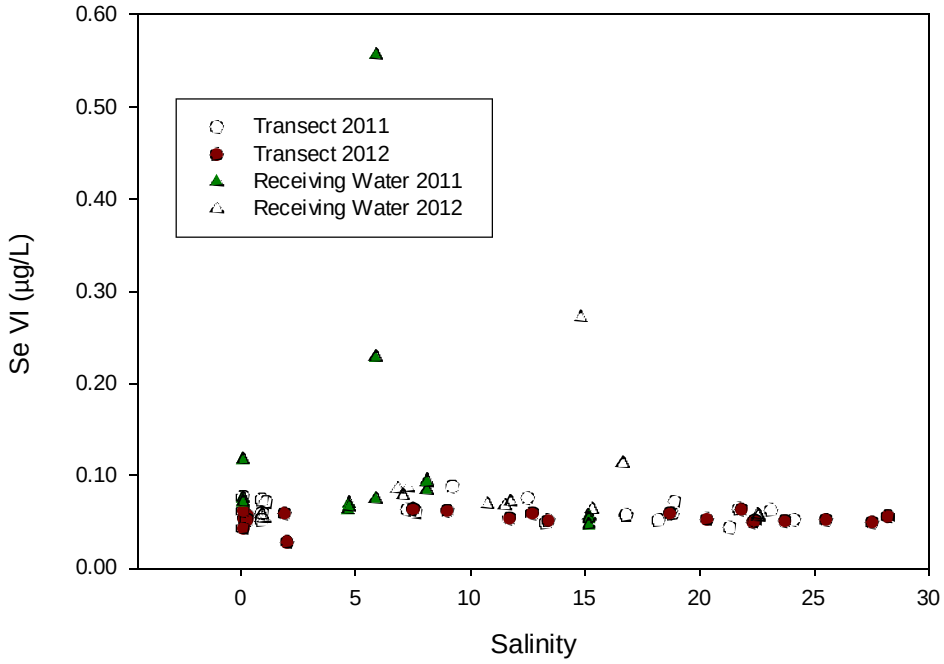

Figure 4-64
Wet weather selenate (SeVI) concentrations across the estuary with data from 2011, 2012 and receiving waters near the five refinery outfalls.

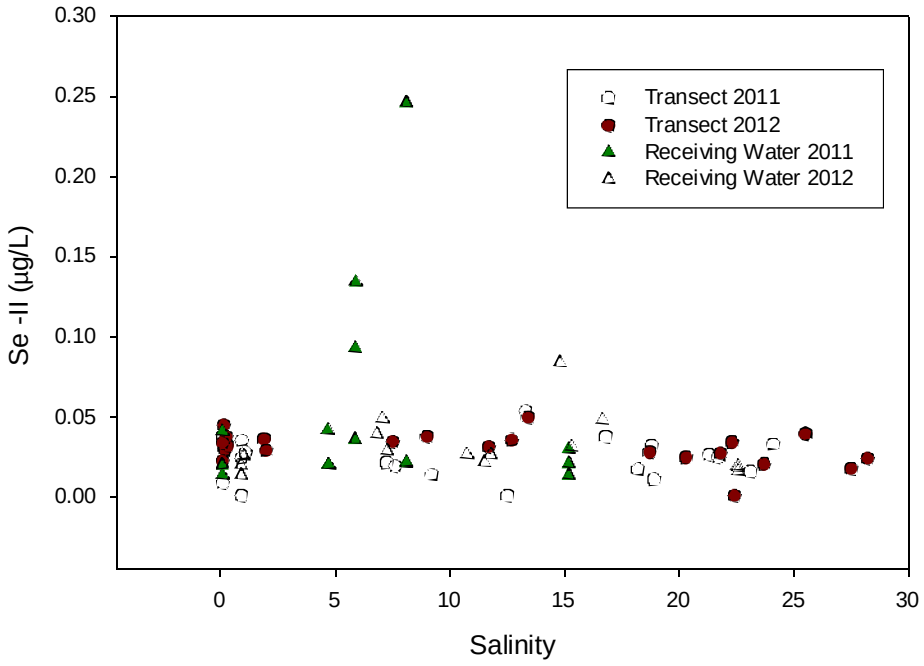

Figure 4-65
Wet weather organic selenium (Se-II) concentrations across the estuary with data from 2011, 2012 and receiving waters near the five refinery outfalls.

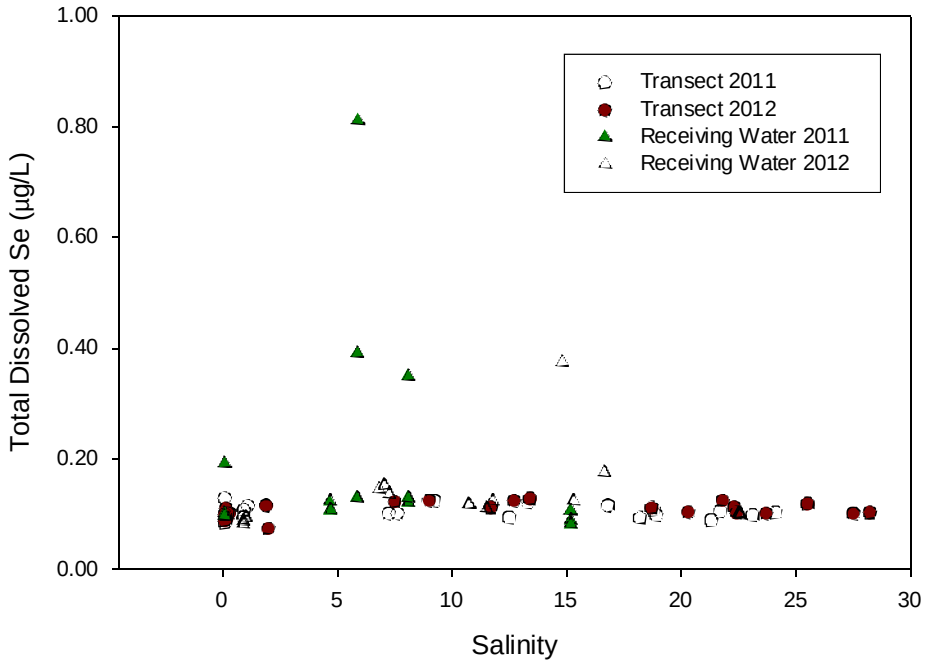

Figure 4-66
Wet weather total dissolved selenium concentrations across the estuary with data from 2011, 2012 and receiving waters near the five refinery outfalls.

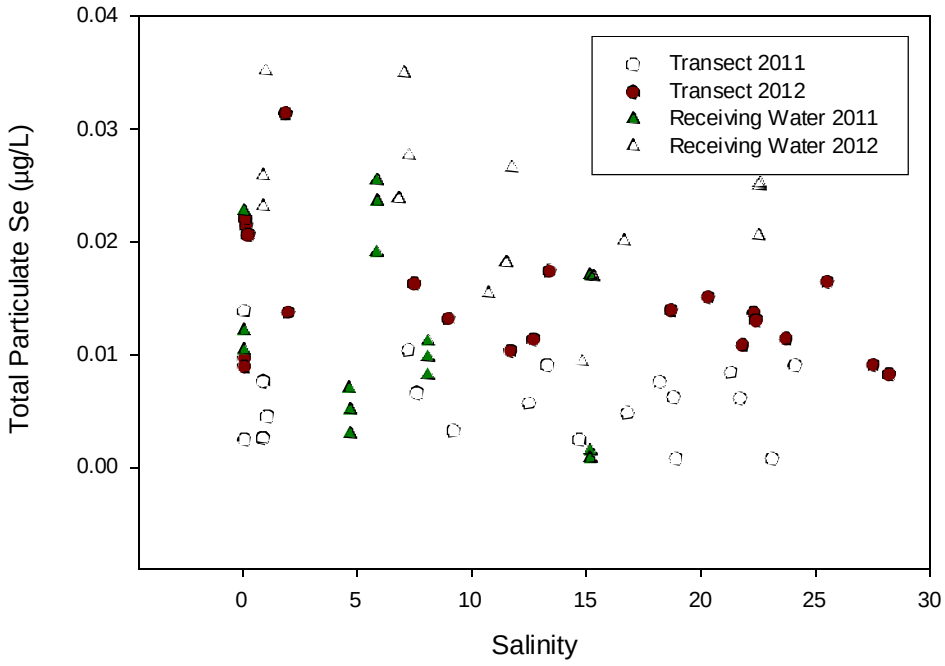

Figure 4-67
Wet weather total particulate selenium concentrations across the estuary with data from 2011, 2012 and receiving waters near the five refinery outfalls.

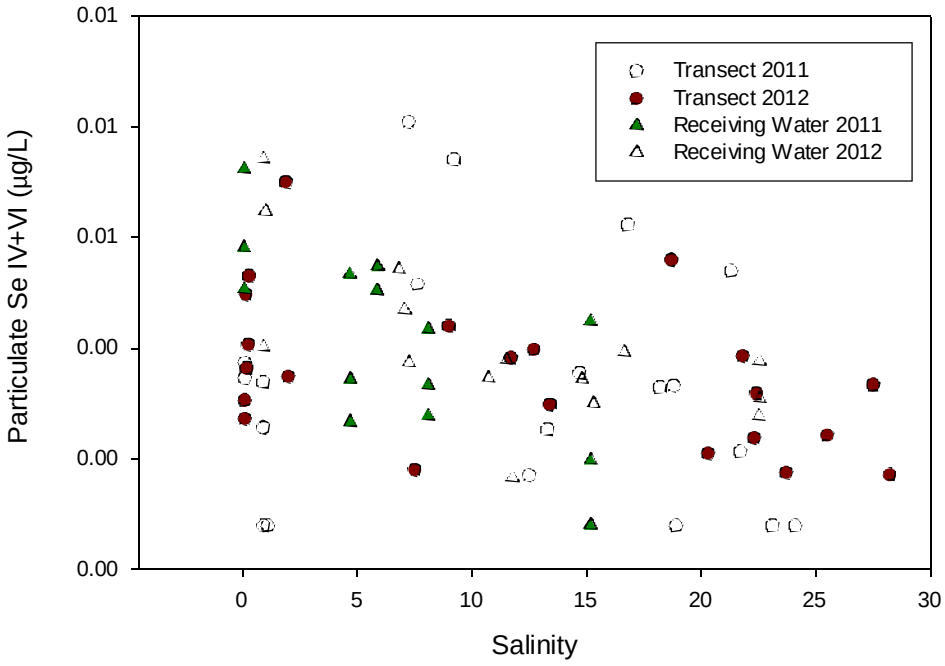

Figure 4-68
Wet weather particulate adsorbed selenite + selenate concentrations across the estuary with data from 2011, 2012 and receiving waters near the five refinery outfalls.

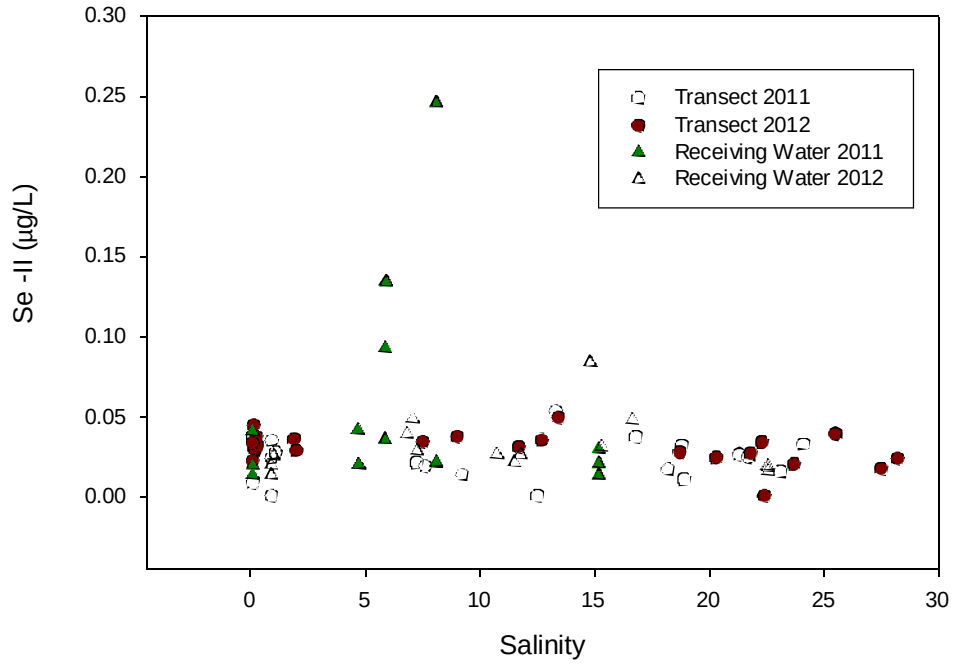

Figure 4-69
Wet weather particulate organic selenium concentrations across the estuary with data from 2011, 2012 and receiving waters near the five refinery outfalls.

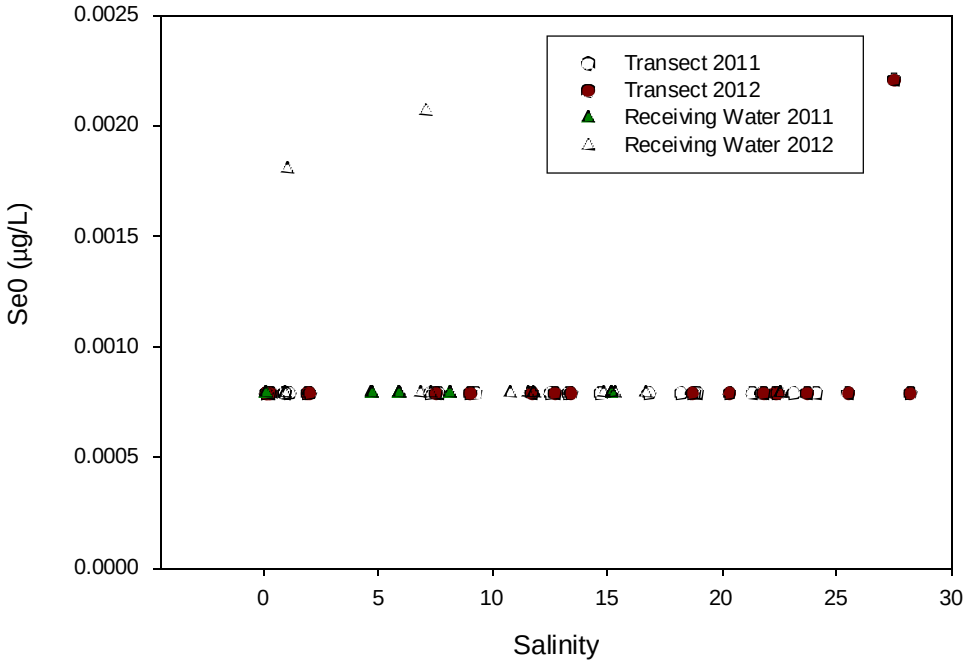

Figure 4-70
Wet weather particulate adsorbed selenite + selenate concentrations across the estuary with data from 2011, 2012 and receiving waters near the five refinery outfalls.

4.5 Summary of Transect Data

The following set of plots was prepared to allow comparison of transect sampling results across the four sampling events in 2010, 2011, and 2012, plus the 1999 data previously reported by Cutter and Cutter (2004) and Doblin et al. (2006). Dry and wet season data are shown on the same plot. The plots are shown for the following quantities and key findings discussed below:

- Phosphate
- Nitrate+nitrite
- Silica
- Chlorophyll a
- Total suspended material
- Dissolved selenite
- Dissolved selenate
- Dissolved organic selenide
- Dissolved total selenium
- Particulate selenate plus selenite
- Particulate organic selenide
- Particulate elemental Selenium
- Particulate total selenium

Nutrient concentrations (phosphate and nitrate plus nitrite) are elevated in the San Joaquin River inflows and are lower in offshore waters. The nitrogen species concentrations were relatively uniform over the six sampling events, although the phosphate concentrations were more variable. Phosphate concentrations were slightly higher in the dry period, especially in September 2010. Silicate concentrations were elevated at the riverine boundaries and lower in the offshore stations. Concentrations over the six sampling events were broadly comparable. Chlorophyll a concentrations were similar across seasons, with March 2011 values being higher than other months. TSM concentrations were higher in the September 2010 and April 2012 sampling events compared to riverine inputs. For the other events, TSM values were lower than the median riverine inputs. Offshore concentrations were much lower than estuarine and riverine stations.

Dissolved selenium concentrations were elevated at Vernalis for selenite and selenate. Offshore concentrations of selenite were similar to concentrations in the Sacramento River at Freeport, although higher concentrations observed through the estuary. Selenate concentrations, in contrast, were higher in the offshore station than the Freeport concentrations, and similar to median values in the estuary. Selenide concentrations were low in offshore waters, but at similar levels in Freeport and Vernalis. Concentrations within the estuary were more variable than the selenate and selenite concentrations. Median selenide concentrations were midway between selenite and selenate concentrations in the estuary. Total selenium concentrations were similar across the six sampling events and substantially higher in the Vernalis inflow.

Particulate selenium concentrations were about an order of magnitude lower than dissolved phase concentrations. Adsorbed selenate and selenite concentrations were elevated at Vernalis compared to Freeport. Estuary station concentrations for this component were similar across seasons, and offshore concentrations were near the detection limit. Elemental selenium concentrations varied across sampling event, although there was no clear seasonal pattern. The

highest concentrations were observed in September 2010, and the lowest concentrations in March 2011 and April 2011. Offshore concentrations of elemental selenium were relatively high, and higher than in-estuary concentrations for most sampling events. Elemental selenium was the largest contributor to particulate selenium in the offshore samples. Total particulate selenium concentrations were highly variable across sampling events with relatively high concentrations in both the Freeport and Vernalis stations. The lowest concentrations were noted in March 2011 and the highest concentrations in April 2012. When examined in units of µg/g (Figure 4-84), the concentrations appear to be higher in the November 1999 and October 2011 events, and higher in both riverine and offshore stations compared to the median estuary concentrations.

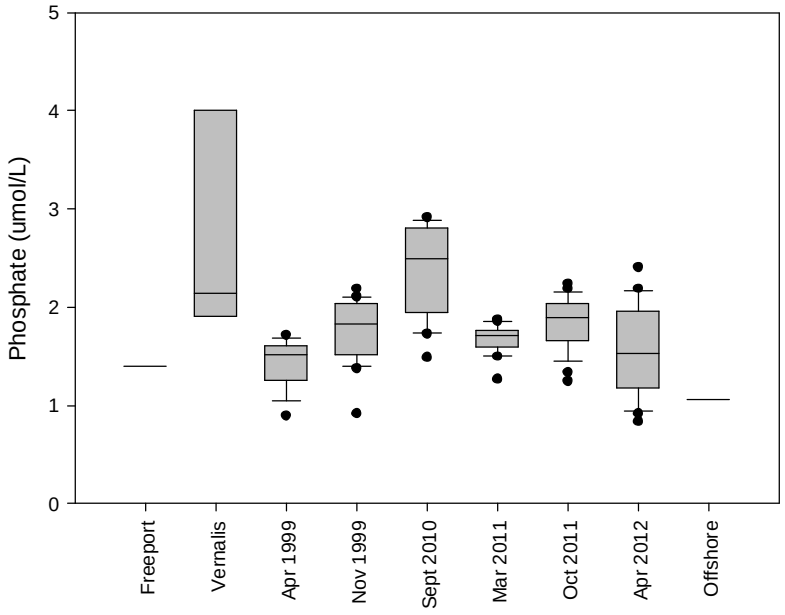

Figure 4-71
Phosphate across sampling events in this study (2010, 2011, 2012) and previous efforts (1999) by Cutter and Cutter (2004) and Doblin et al. (2006).

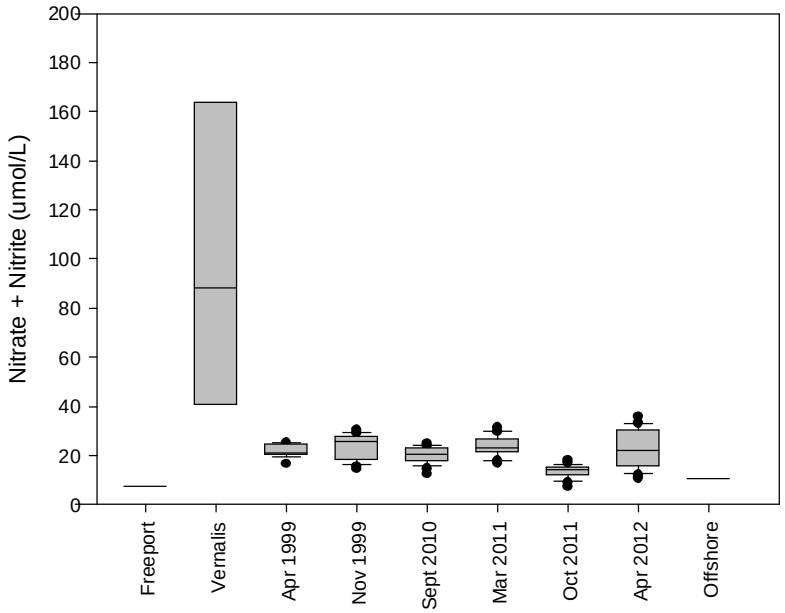

Figure 4-72
Nitrate plus nitrite across sampling events in this study (2010, 2011, 2012) and previous efforts (1999) by Cutter and Cutter (2004) and Doblin et al. (2006).

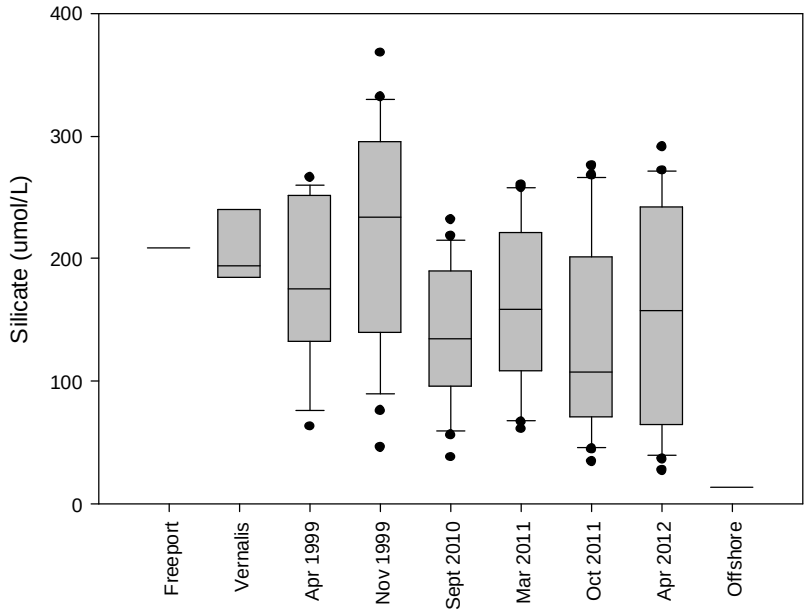

Figure 4-73
Silicate across sampling events in this study (2010, 2011, 2012) and previous efforts (1999) by Cutter and Cutter (2004) and Doblin et al. (2006).

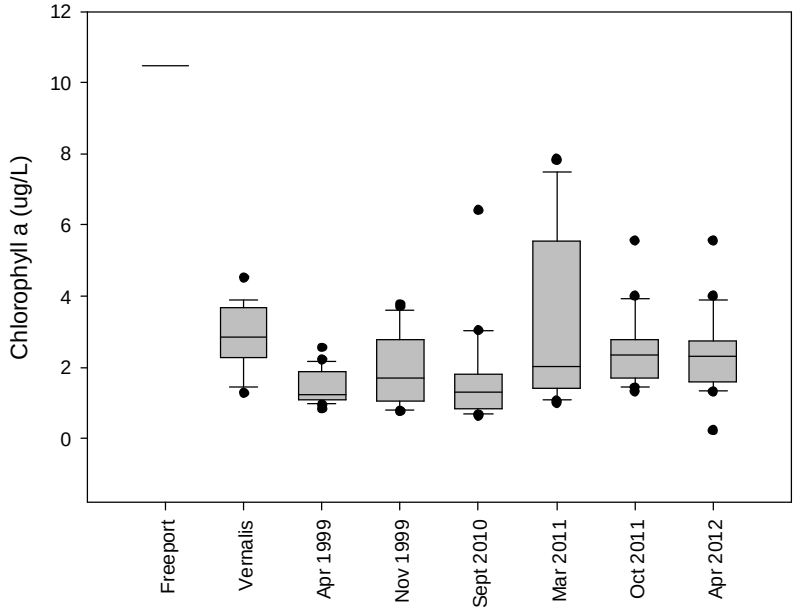

Figure 4-74
Chlorophyll a across sampling events in this study (2010, 2011, 2012) and previous efforts (1999) by Cutter and Cutter (2004) and Doblin et al. (2006).

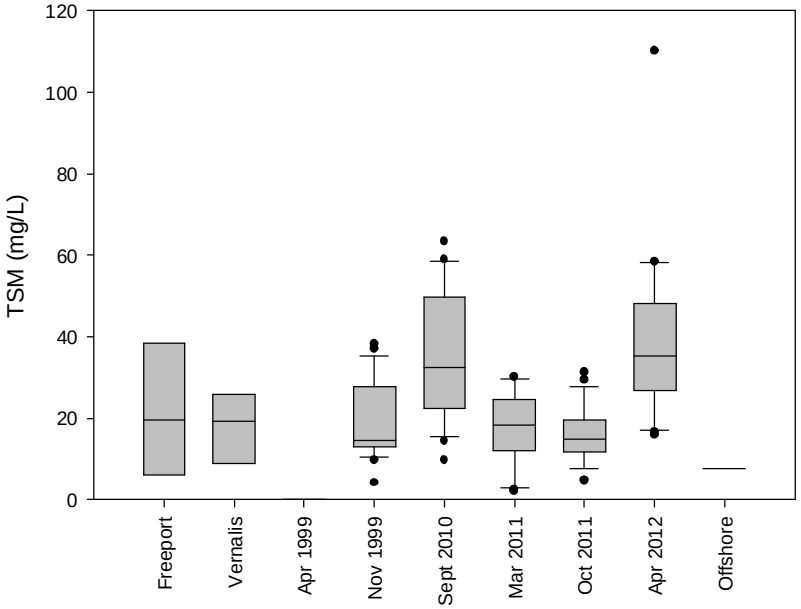

Figure 4-75
Total Suspended Material (TSM) across sampling events in this study (2010, 2011, 2012) and previous efforts (1999) by Doblin et al. (2006).

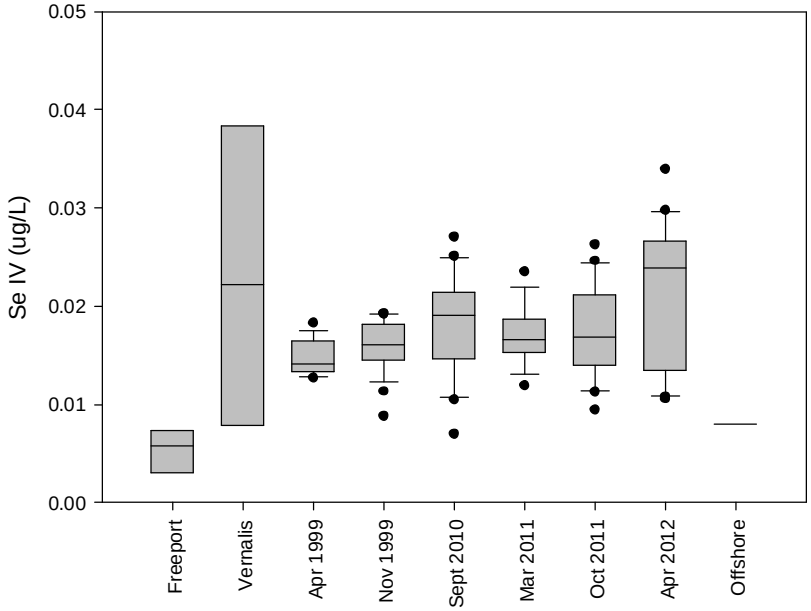

Figure 4-76
Dissolved selenite across sampling events in this study (2010, 2011, 2012) and previous efforts (1999) by Cutter and Cutter (2004) and Doblin et al. (2006).

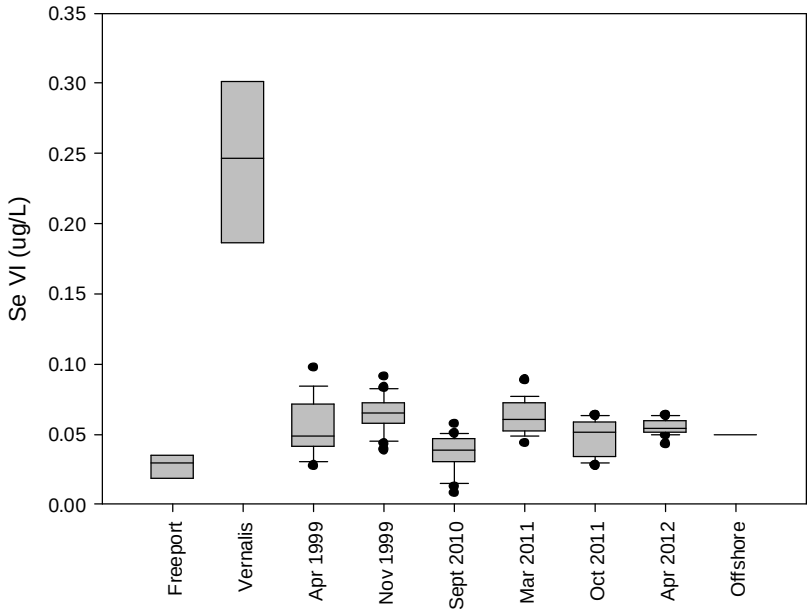

Figure 4-77
Dissolved selenate across sampling events in this study (2010, 2011, 2012) and previous efforts (1999) by Cutter and Cutter (2004) and Doblin et al. (2006).

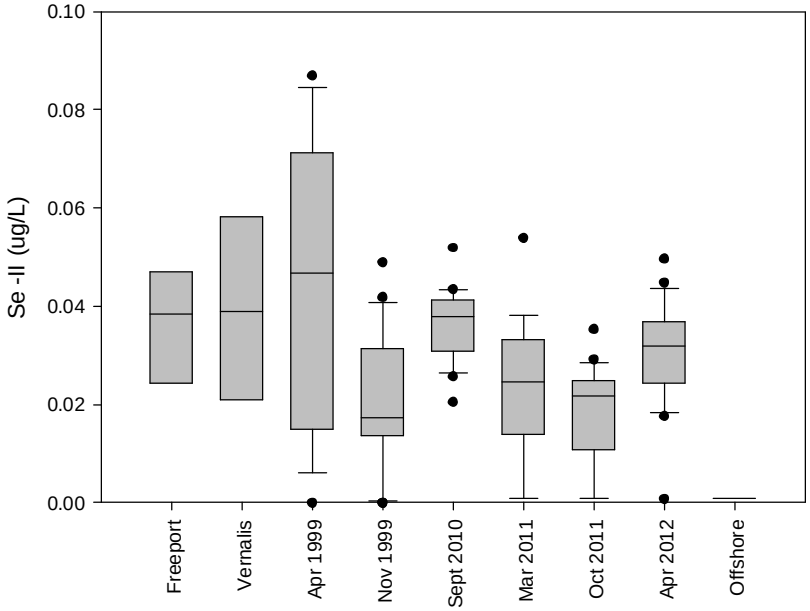

Figure 4-78
Dissolved organic selenide across sampling events in this study (2010, 2011, 2012) and previous efforts (1999) by Cutter and Cutter (2004) and Doblin et al. (2006).

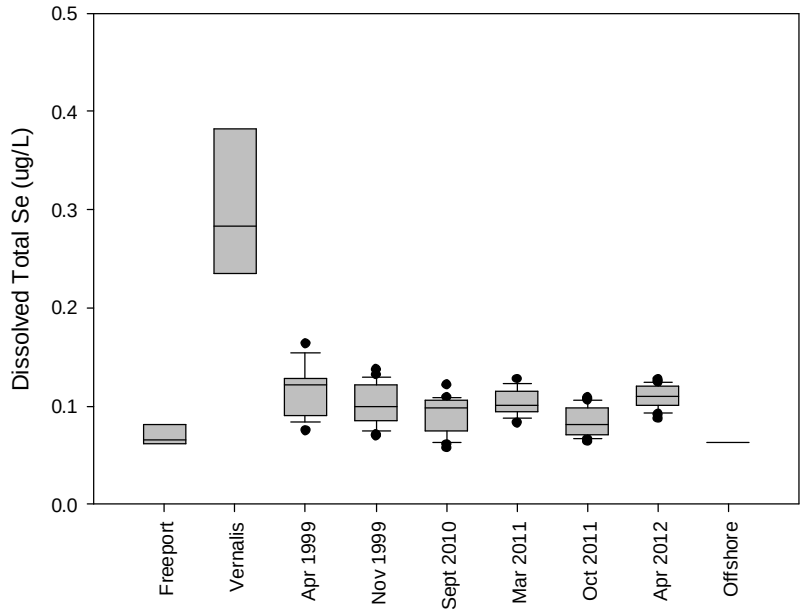

Figure 4-79
Dissolved total selenium across sampling events in this study (2010, 2011, 2012) and previous efforts (1999) by Cutter and Cutter (2004) and Doblin et al. (2006).

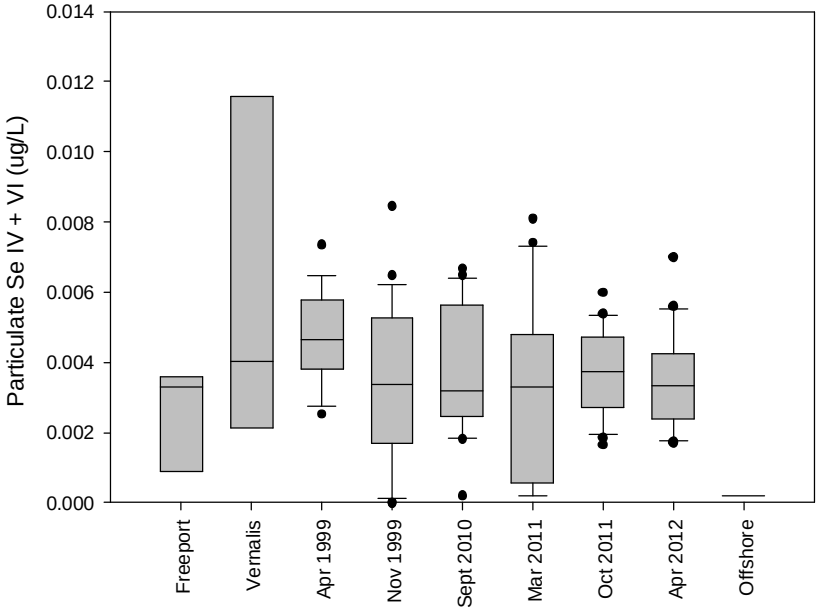

Figure 4-80
Particulate selenate plus selenite across sampling events in this study (2010, 2011, 2012) and previous efforts (1999) by Cutter and Cutter (2004) and Doblin et al. (2006).

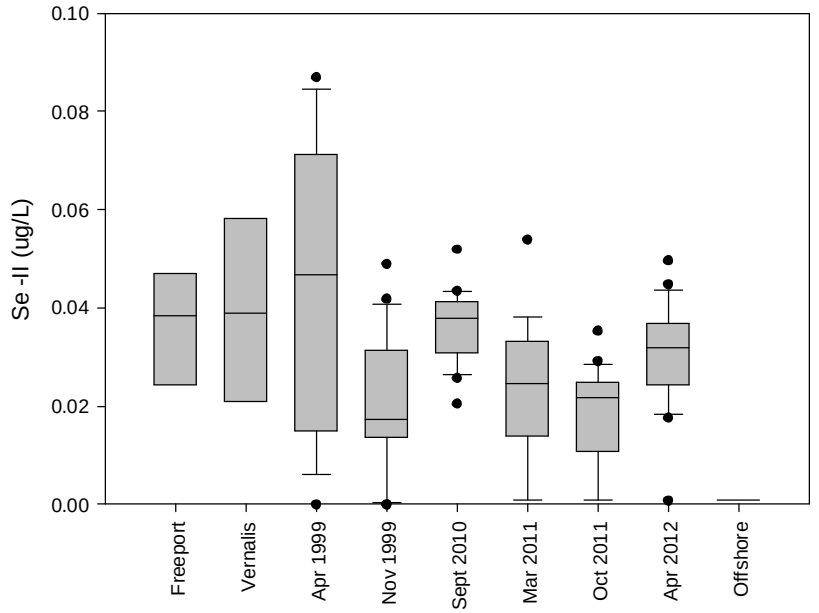

Figure 4-81
Particulate organic selenide across sampling events in this study (2010, 2011, 2012) and previous efforts (1999) by Cutter and Cutter (2004) and Doblin et al. (2006).

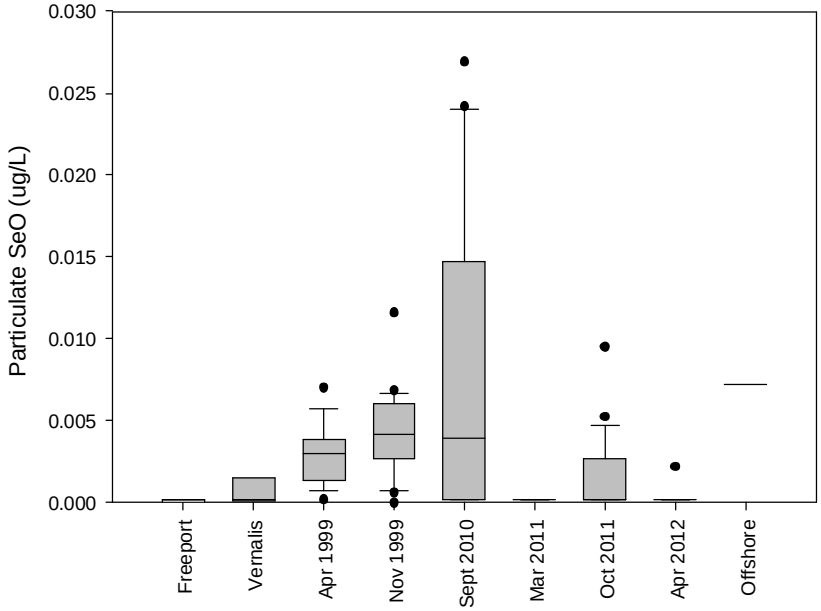

Figure 4-82
Particulate elemental selenium across sampling events in this study (2010, 2011, 2012) and previous efforts (1999) by Cutter and Cutter (2004) and Doblin et al. (2006).

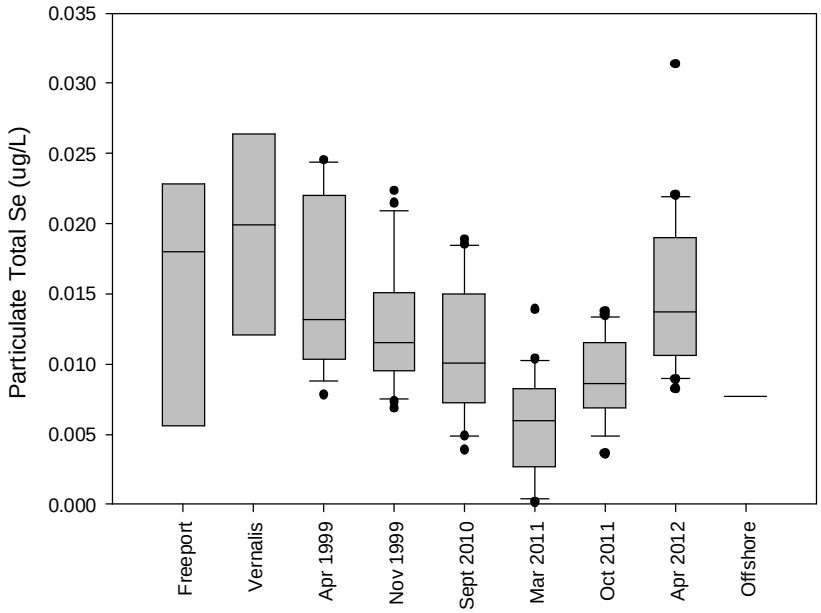

Figure 4-83
Particulate total selenium (ug/L) across sampling events in this study (2010, 2011, 2012) and previous efforts (1999) by Cutter and Cutter (2004) and Doblin et al. (2006).

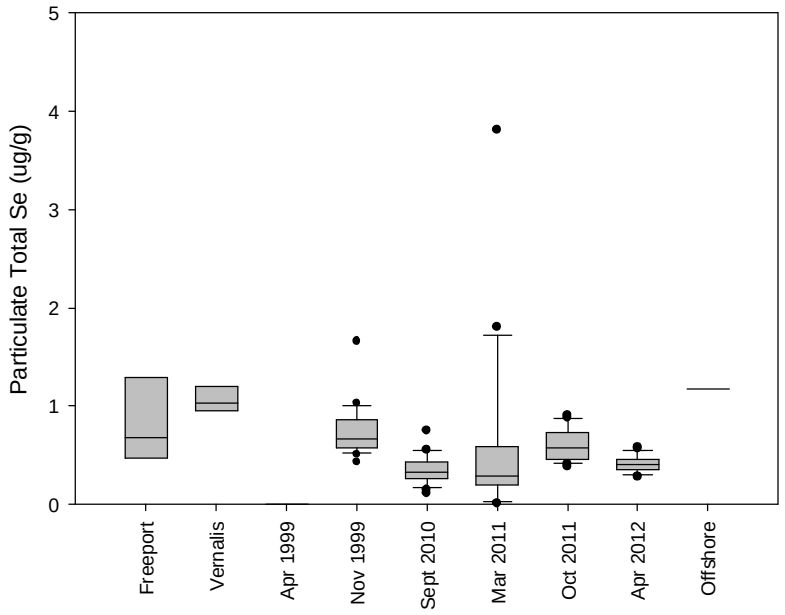

Figure 4-84
Particulate total selenium (ug/g) across sampling events in this study (2010, 2011, 2012) and previous efforts (1999) by Cutter and Cutter (2004) and Doblin et al. (2006).

4.6 Refinery Effluent Data

Dissolved and particulate selenium by species were also sampled directly from the five refinery effluents on a monthly basis (Table B-12). The dissolved selenium concentrations from refinery effluents samples are shown by month in Figure 4-85 to Figure 4-88. Selenite concentrations in refinery effluents show variations over time and among refineries. Concentrations are generally below 10 µg/L, with median concentrations generally below 4 µg/L (Figure 4-85). Selenate concentrations in the refinery effluents generally range between 2–18 µg/L, with concentrations varying among refineries and over time. Generally median selenate concentrations were below 10 µg/L for most of the time periods sampled (Figure 4-86). Organic selenide showed the same range of concentrations as selenite, with concentrations generally ranging between 1–9 µg/L, and showed even larger variations over the sampling time periods. Median organic selenide concentrations ranged from 1 µg/L to 7.5 µg/L (Figure 4-87). Total dissolved selenium concentrations in the refinery effluents generally ranged between 5–30 µg/L(Figure 4-88). Median total dissolved selenium concentrations ranged between 7.5–22.5 µg/L.

Among the particulate selenium species sampled, particulate organic selenide showed concentrations ranging from 0.02 to 0.3 µg/L, particulate elemental selenium from 0.05 – 0.35 µg/L, and particulate selenite and selenate showed the lowest concentrations, generally below 0.06 µg/L (Figure 4-89 to Figure 4-91). Total particulate selenium concentrations in refinery effluents ranged from 0.03-0.6 µg/L (Figure 4-92). When expressed as µg/g, total particulate selenium concentrations generally ranged from 10-190 µg/g (Figure 4-93). Speciation of particulate selenium in refinery effluents was dominated by elemental selenium, followed by particulate organic selenide and particulate selenite and selenate. TSM concentrations generally ranged between 2–20 mg/L in the effluents sampled (Figure 4-94).

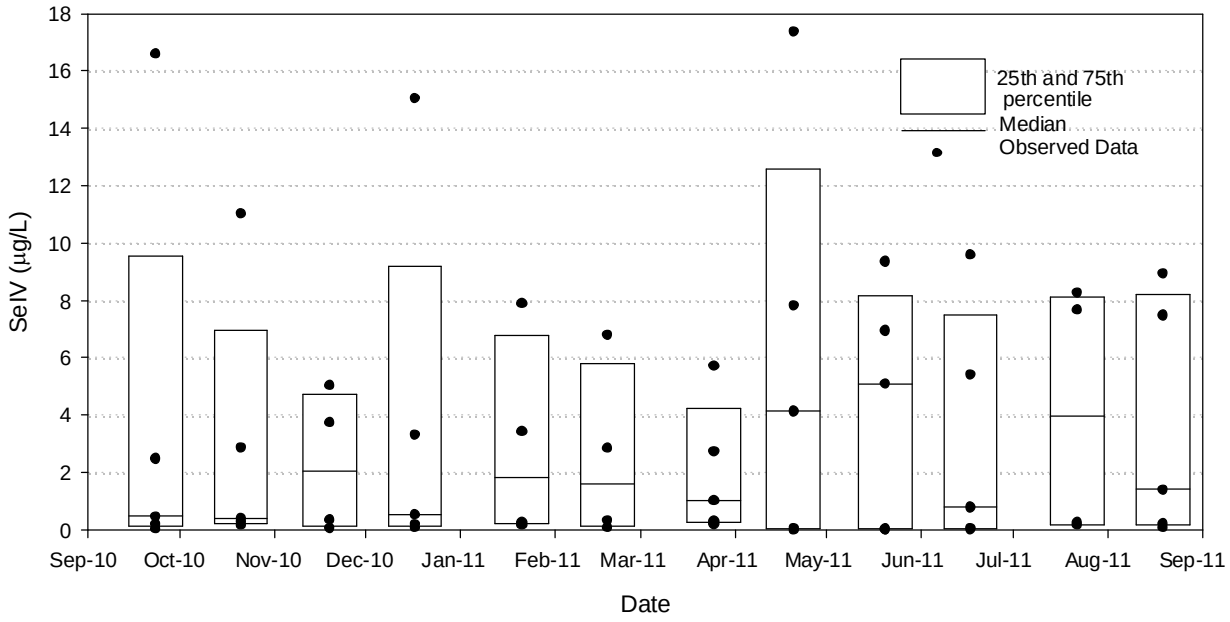

Figure 4-85
Dissolved selenite (SeIV) concentrations sampled in effluents of the five refineries during 2010–2011. For the first sampling event (Sept 2010), one of the five refineries was sampled in the first week of October but is shown in the first box in this plot and following plots. Each refinery sample is shown as a single data point.

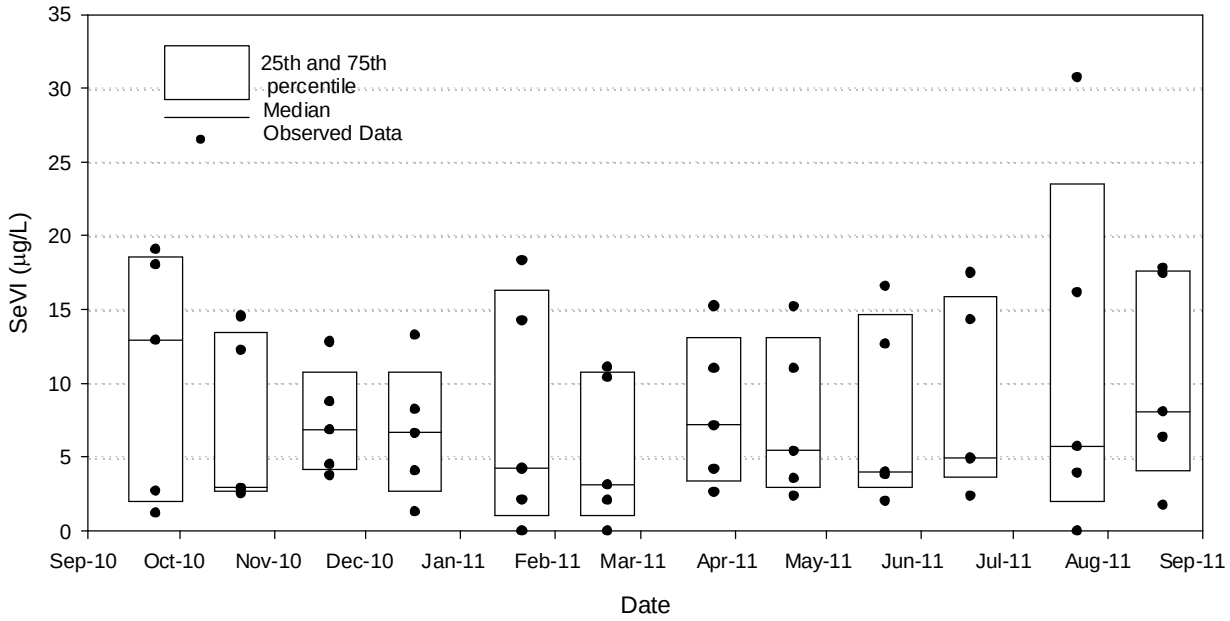

Figure 4-86
Dissolved selenate (SeVI) concentrations sampled in effluents of the five refineries during 2010–2011.

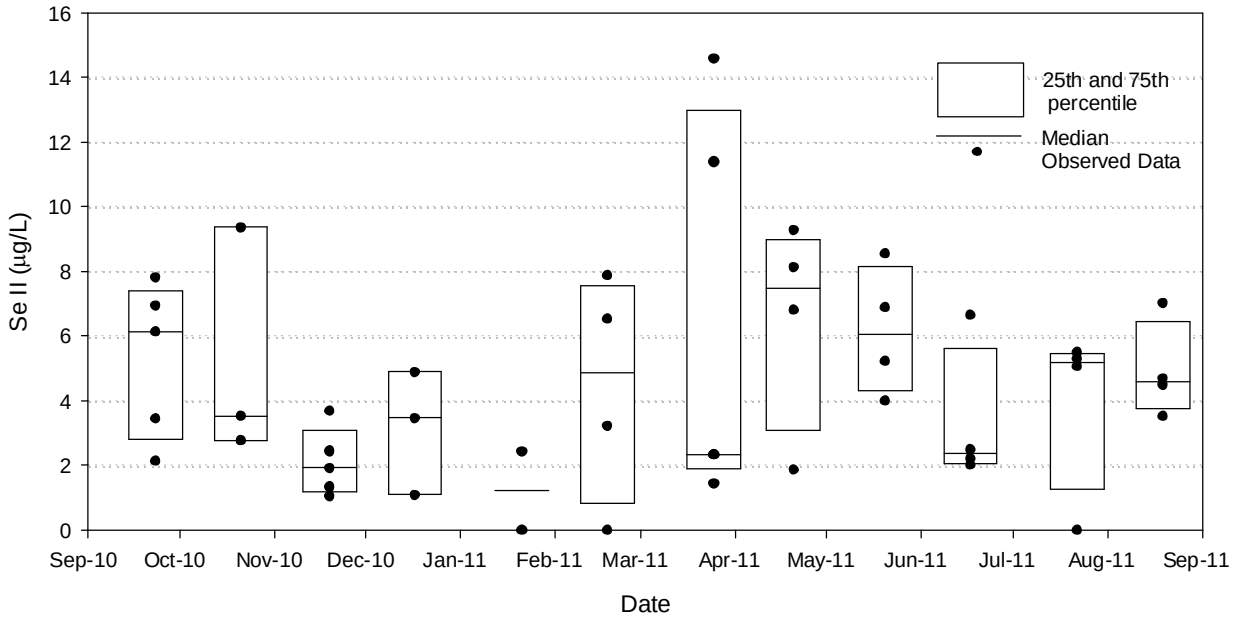

Figure 4-87
Dissolved organic selenide (Se-II) concentrations sampled in effluents of the five refineries during 2010–2011.

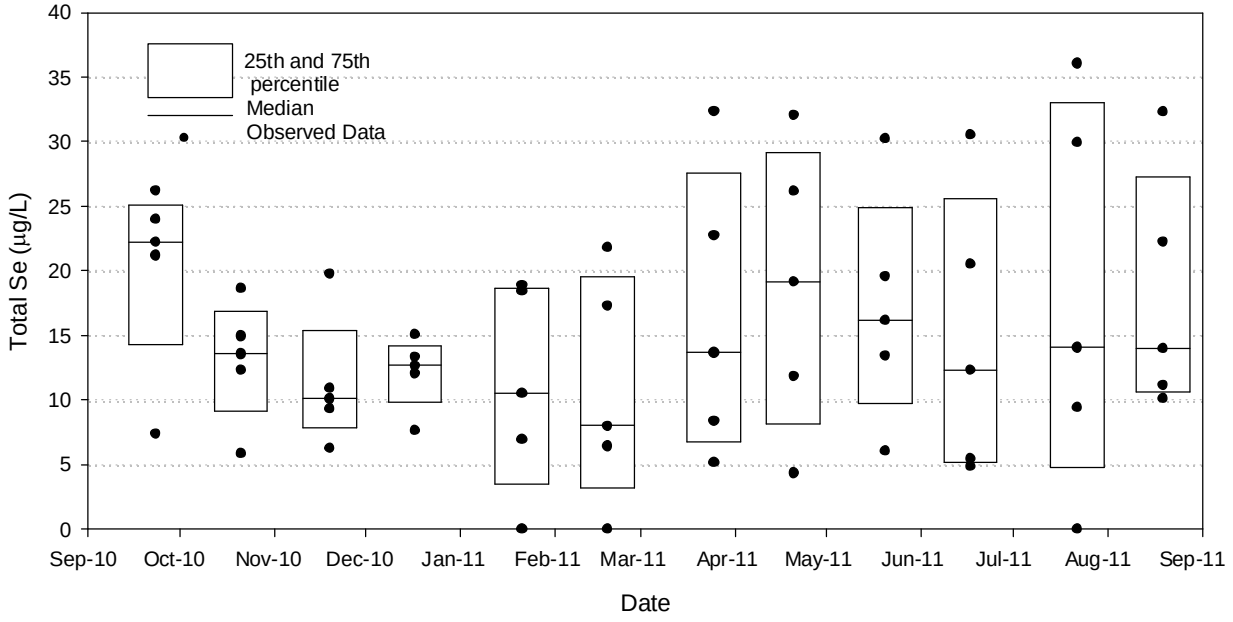

Figure 4-88
Dissolved total selenium (Se) concentrations sampled in effluents of the five refineries during 2010–2011.

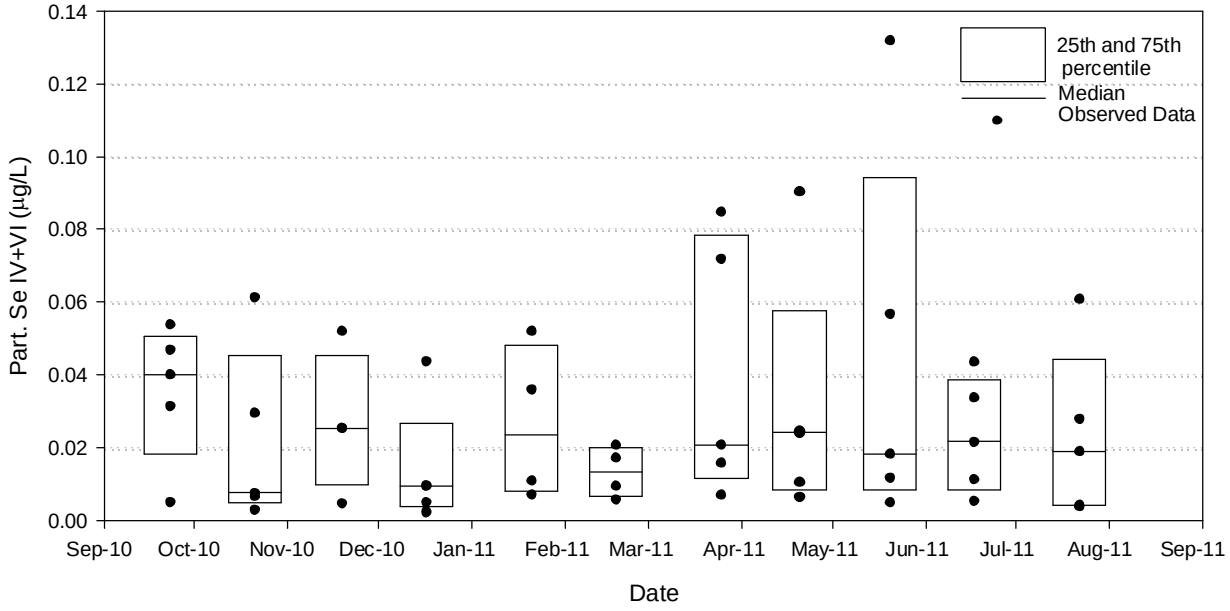

Figure 4-89
Particulate adsorbed selenite and selenate (Part. SeIV+VI) concentrations sampled in effluents of the five refineries during 2010–2011.

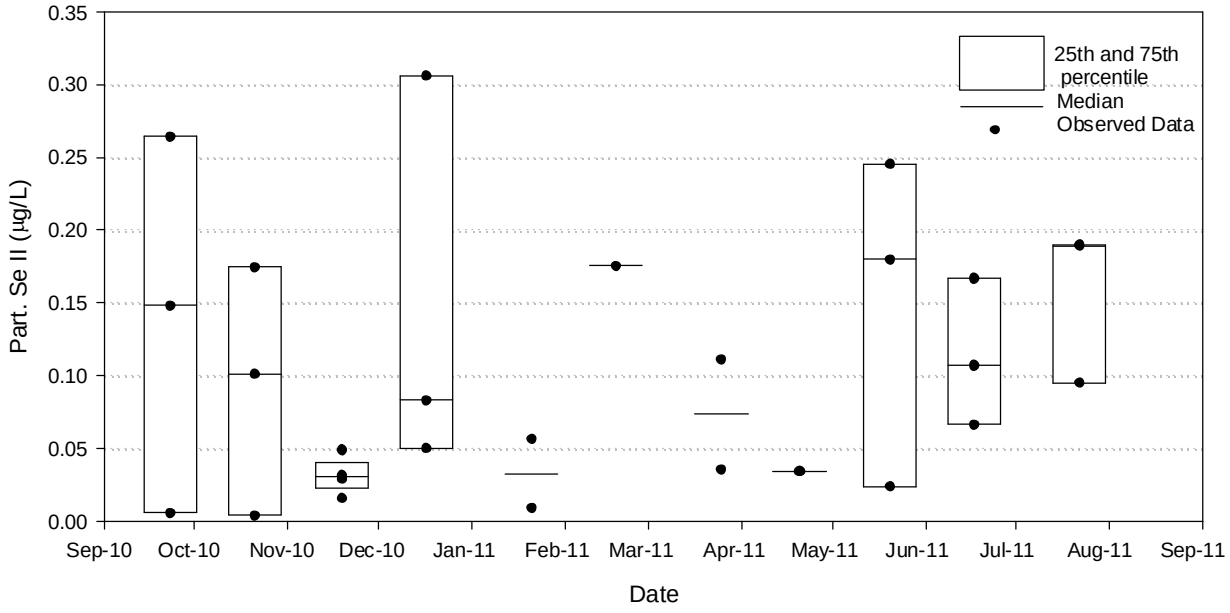

Figure 4-90
Particulate organic selenide (Part. Se-II) concentrations sampled in effluents of the five refineries during 2010–2011.

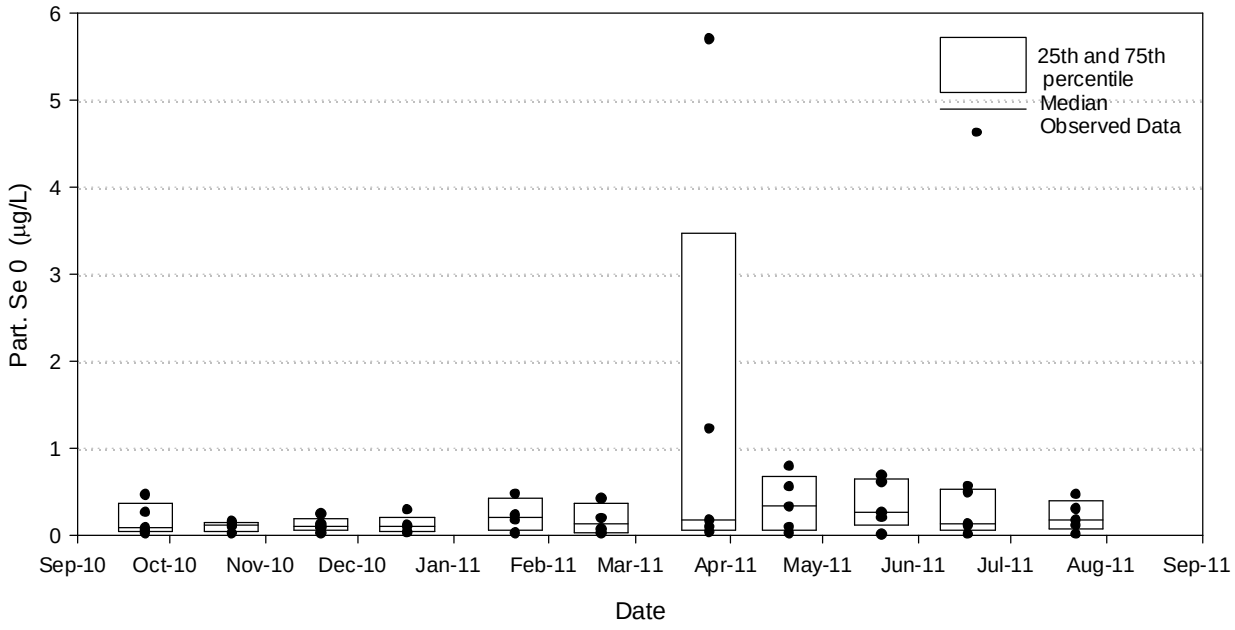

Figure 4-91
Particulate elemental selenium (Part. Se0) concentrations sampled in effluents of the five refineries during 2010–2011.

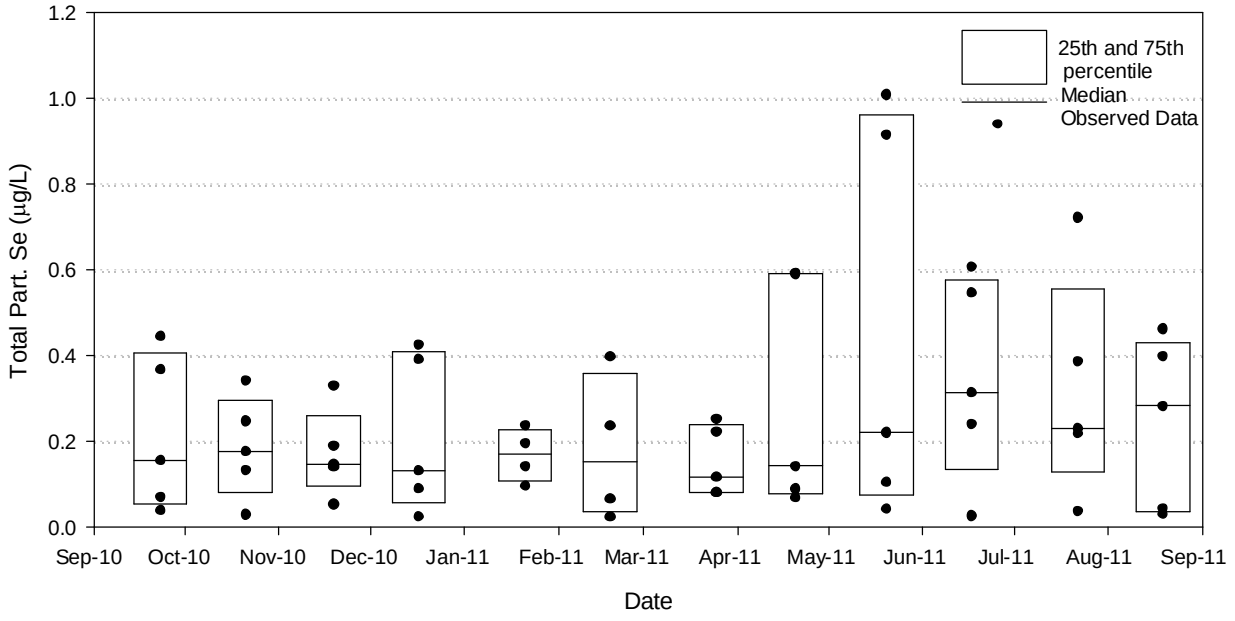

Figure 4-92
Particulate total selenium concentrations in µg/l sampled in effluents of the five refineries during 2010–2011.

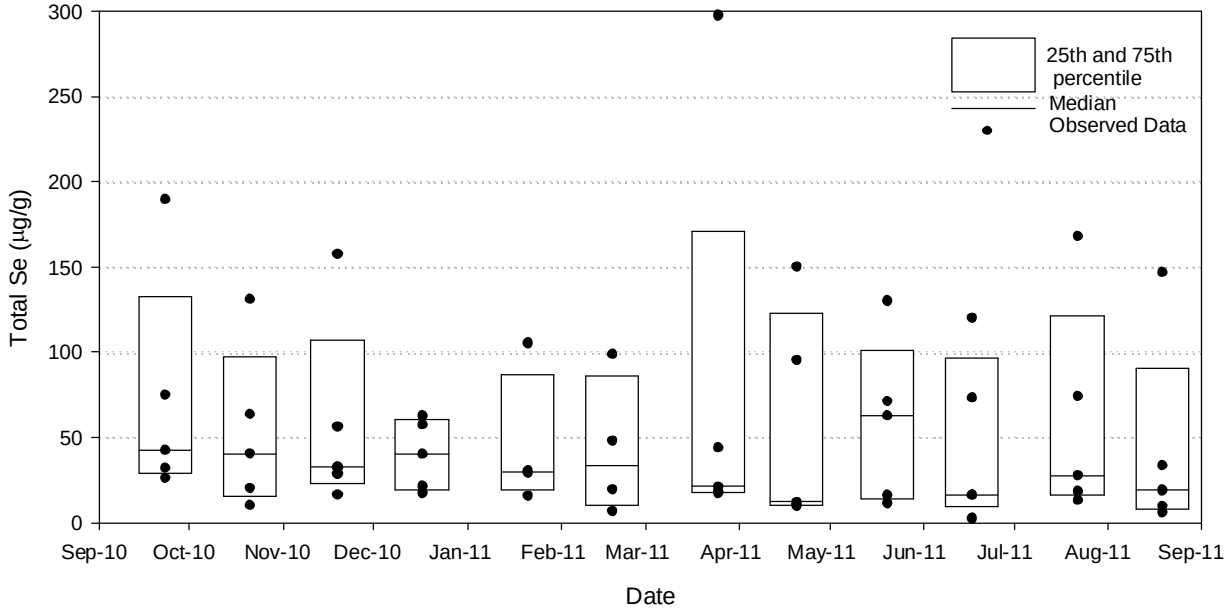

Figure 4-93
Particulate total selenium concentrations in µg/g sampled in effluents of the five refineries during 2010–2011.

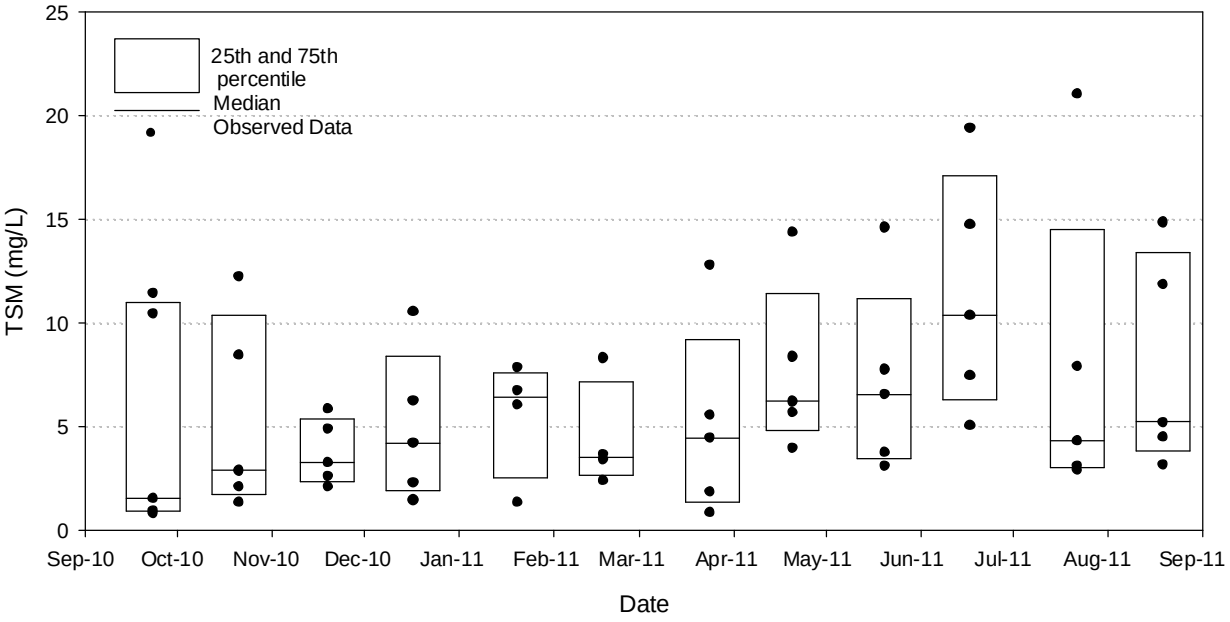

Figure 4-94
TSM concentrations sampled in effluents of the five refineries during 2010–2011.

5 Selenium Modeling Update

A previously developed numerical model of selenium transport and transformation in North San Francisco Bay (Tetra Tech, 2010; Chen et al., 2012) was applied with updated flow and selenium load inputs up to April 2012 to estimate concentrations in the bay and to compare against observations described in Section 4. The modeling was performed with transformation rates that were similar to those used in the previous work, with the exception of phytoplankton uptake rates, and the values estimated are thus a reflection of changes in the inputs. The components modeled here include salinity, TSM, dissolved selenium species (selenate, SeVI; selenite, SeIV; organic selenide, OrgSe), and particulate selenium species (selenate plus selenite, PSeIV+VI; organic selenide, POrgSe; and elemental selenium, PSe0). A reasonable match between the model-estimated values and observations provides support for its use in planning and management of selenium in the bay under current and future conditions. This chapter describes the process used for updating the model inputs and compares the outputs to observations reported in Chapter 4.

5.1 Flow and Hydrodynamic Modeling

Precipitation and Evaporation

Precipitation input to the bay was extended to August 2012 using daily data from California Irrigation Management Information System (CIMIS; *http://wwwcimis.water.ca.gov/cimis/data.jsp*) at a station near San Francisco Bay (Station #109). Evaporation records were extended to August 2012 using data from the same CIMIS station.

Flow

Flow from the Sacramento River to the bay was extended to August 2012 using DAYFLOW data from the Interagency Ecological Program (IEP; *http://www.water.ca.gov/dayflow/output/)* and California Data Exchange Center (CDEC; *http://cdec.water.ca.gov/).* The San Joaquin River flow was calculated as the difference between the Delta outflow (Net Delta Outflow Index, NDOI) and Rio Vista flow.

Tributaries

The Napa River flow was extended to June 2012 using daily flow records from the USGS (*http://waterdata.usgs.gov/nwis*) at Napa River (USGS11458000, Napa River near Napa, CA).

5.2 Physical Parameters

Salinity, TSM and Chlorophyll a

Approximately 21 stations in the NSFB were sampled by USGS during monthly basis through cruises for salinity, TSM, and chlorophyll a (*http://sfbay.wr.usgs.gov/access/wqdata*/). These data

were used in addition to the transect sampling to evaluate model simulations in salinity, TSM, and chlorophyll a for the period of 2009-2012.

5.3 Boundary Conditions

Flow

Flow boundary conditions at Rio Vista and San Joaquin River inputs were extended to August 2012, using data obtained from IEP and CDEC, as discussed above.

Physical Parameters

Boundary conditions for physical parameters (TSM, chlorophyll a) at Rio Vista were extended to June 2012 using observed monthly data at Rio Vista from USGS bay cruises sampling. A more time intensive dataset for TSM and chlorophyll a (e.g., at daily time step) could not be identified at this location. Phytoplankton inputs from San Joaquin River were updated using data from San Joaquin River at Twitchell Island obtained from IEP (*http://www.water.ca.gov/iep/products/data.cfm*) and Jersey Point obtained from SWAMP (*http://www.ceden.us/AdvancedQueryTool*). Boundary conditions for physical parameters at Golden Gate were data collected from USGS bay cruises sampling and from this study.

Selenium Data

San Joaquin River

Total dissolved selenium concentrations at San Joaquin River near Vernalis were updated to 6/29/2010 using the SWAMP dataset, and transect samples collected within this study (Figure 5-1). The speciation of dissolved selenium used for this station was data collected within this study (Figure 5-2). The inputs of particulate selenium from Vernalis were associated with dissolved selenium through Kd values for particulate selenite and selenate and particulate organic selenium, derived based on the observed data. Particulate elemental (PSe0) concentrations from San Joaquin River at Vernalis were constant inputs, as suggested by the data (Figure 5-3). Total particulate selenium concentrations from the San Joaquin River at Vernalis generally ranged from 0.87–1.48 µg/g.

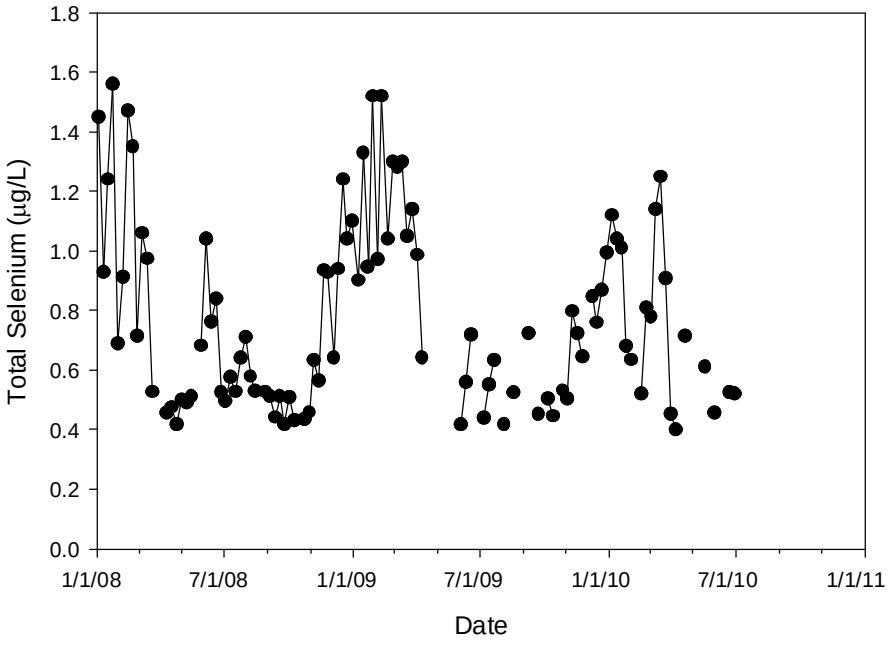

Figure 5-1
Total selenium concentrations at San Joaquin River near Vernalis (data source: SWAMP).

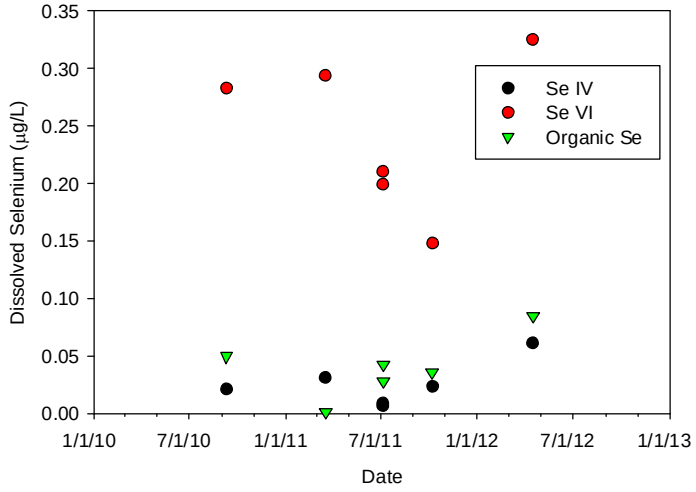

Figure 5-2
Dissolved selenium speciation at San Joaquin River at Vernalis sampled in this study.

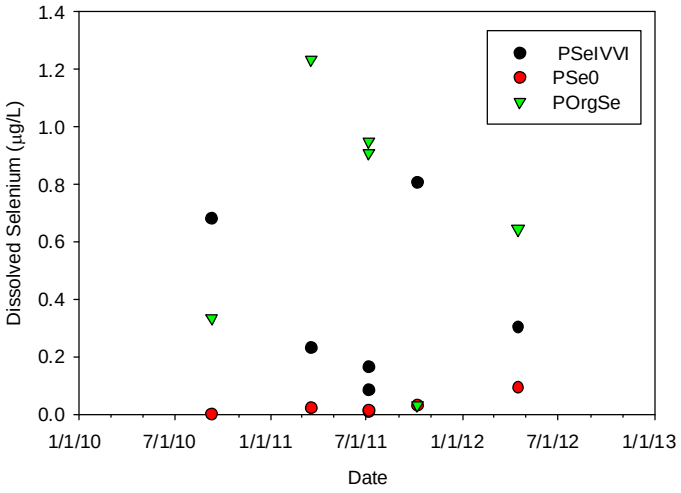

Figure 5-3
Particulate selenium speciation at San Joaquin River at Vernalis sampled in this study.

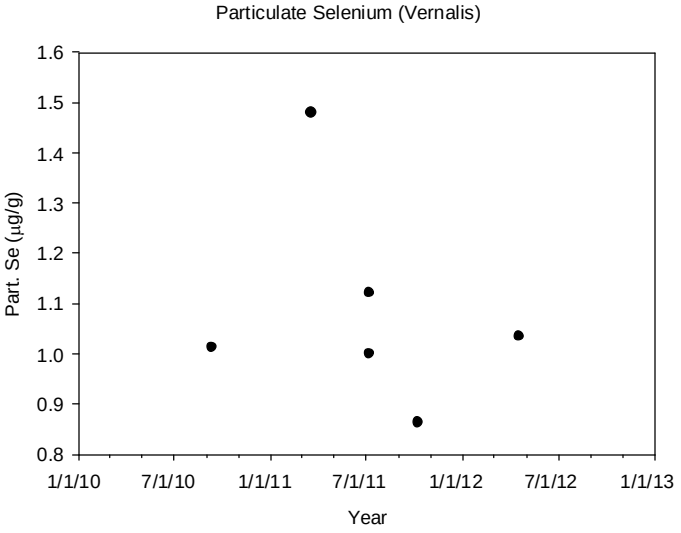

Figure 5-4
Particulate selenium concentrations at San Joaquin River at Vernalis sampled in this study.

Sacramento River

Dissolved selenium concentrations for Sacramento River at Freeport were data collected by Cutter and Cutter (2004) and during this study for different species. A function fitted for each species of the data for model input, similar to approach outlined in Meseck (2002), was used. Particulate selenium concentrations measured at Sacramento River at Freeport ranged from 0.47 – 1.40 µg/g. The inputs of particulate selenium at Freeport were specified using values from the previous study (Tetra Tech, 2010).

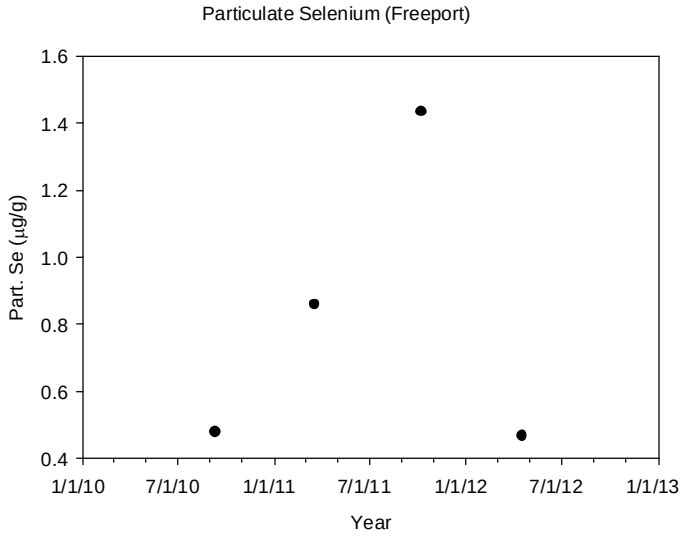

Figure 5-5
Particulate selenium concentrations at Sacramento River at Freeport sampled in this study.

Golden Gate

Dissolved and particulate selenium concentrations measured at Golden Gate from previous studies (Cutter and Cutter, 2004; Doblin et al. 2006) and in this study were used as the boundary concentrations for Golden Gate.

5.4 Inputs from Refineries

Daily total selenium loads from five refineries were extended to 02/2012 or 03/2012 using flow and selenium data for dischargers obtained from SFBRWCB (Figure 5-6).

Effluent from five refineries was sampled on a monthly basis during this study for different dissolved and particulate selenium species, for the period of September 2010–August 2011 (Figure 5-7). This information was used to specify selenium speciation for the refinery inputs for the period of 2010–2011 and the later period. Refinery speciation sampled for the period of 1999–2000 by Cutter and Cutter (2004) was also used in the model for the period of 1999–2000 and for the 2000–2010 period. Since particulate selenium concentrations from the refineries were also sampled, particulate selenium inputs from refineries were also added to the model.

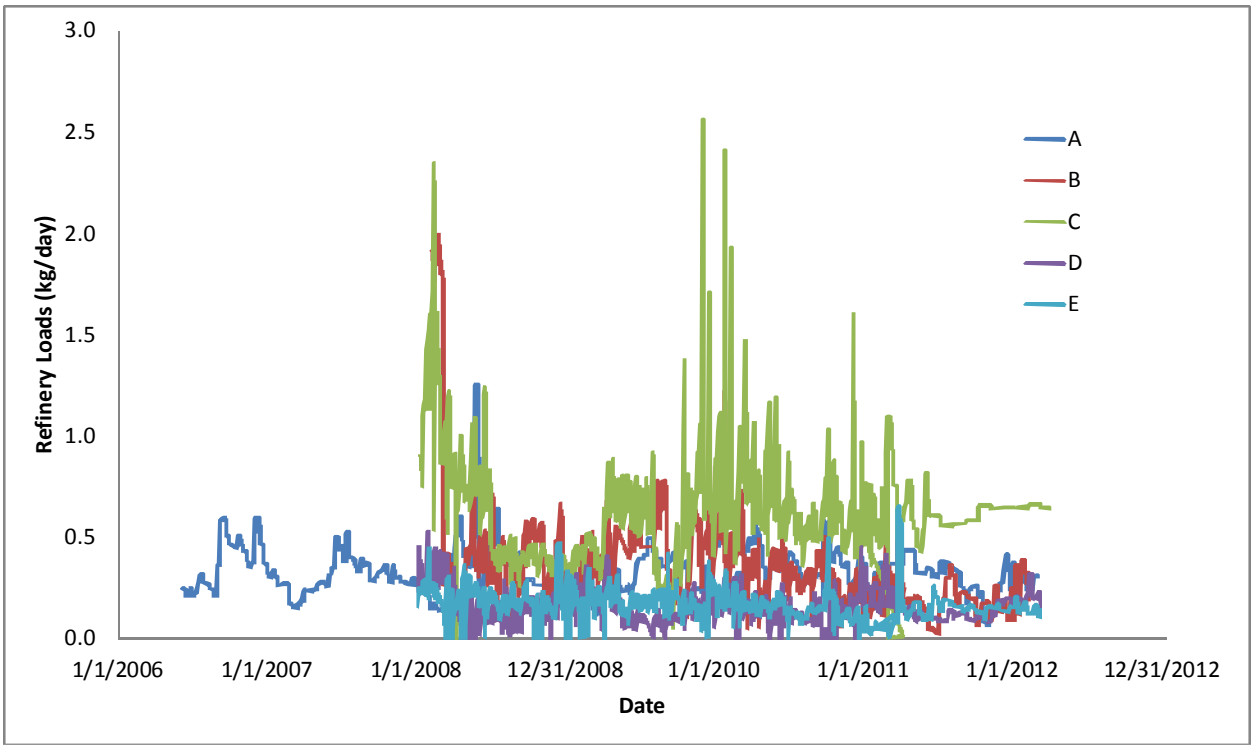

Figure 5-6
Daily total selenium loads from five refineries for the period of 2008-2012.

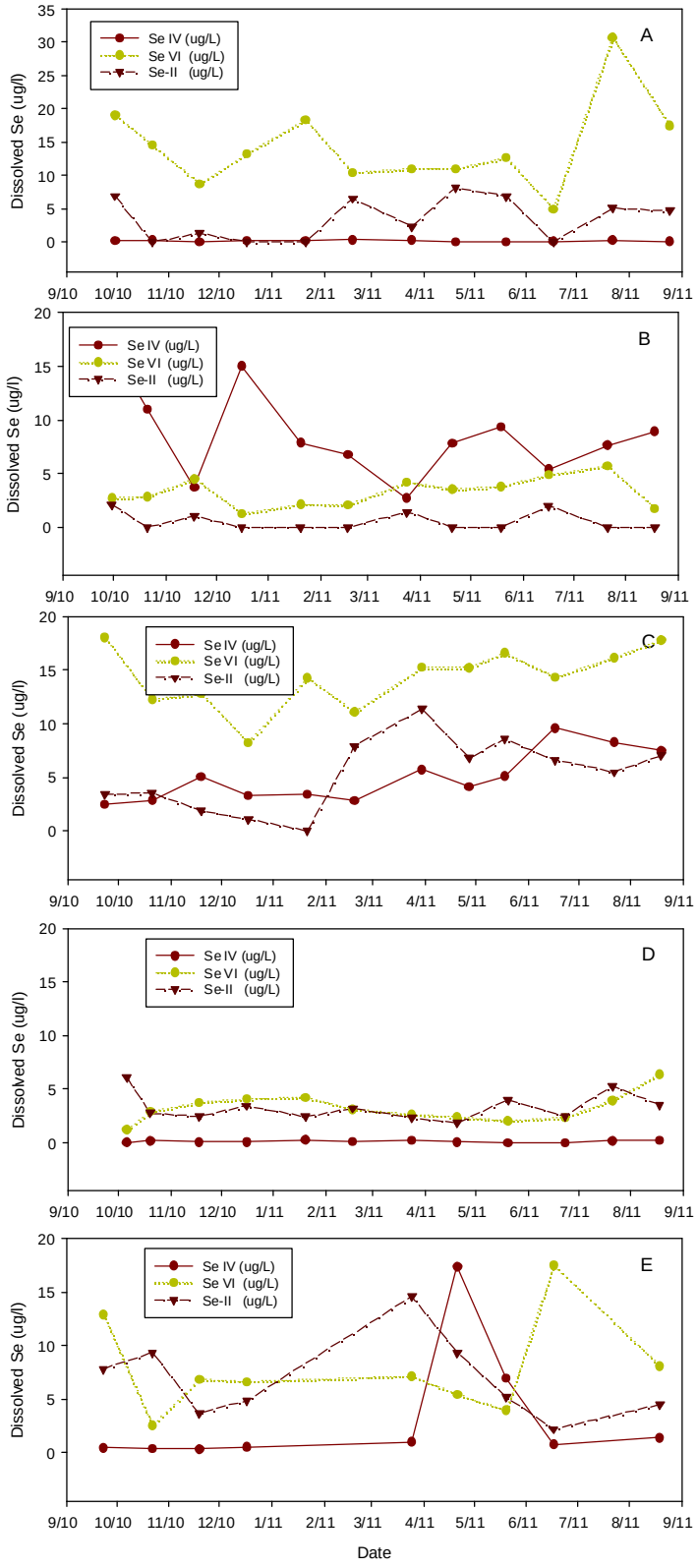

Figure 5-7
Speciation of dissolved selenium in effluents of five refineries sampled during this study.

5.5 Inputs from Municipal and Industrial Dischargers

Unlike the previous modeling effort, where municipal and industrial discharges were specified as constant inputs, time-series inputs were used for this study. Daily total selenium loads for municipal and industrial dischargers were calculated for the period of 2008–2012 and for the period before 2008, using flow and selenium data obtained from SFBRWCB. Daily total selenium loads from the major municipal dischargers are shown in Figure 5-8.

Speciation of selenium from municipal and industrial discharges was similar to refinery discharges, with SeIV(5%), SeVI (75%), and OrgSe (20%).

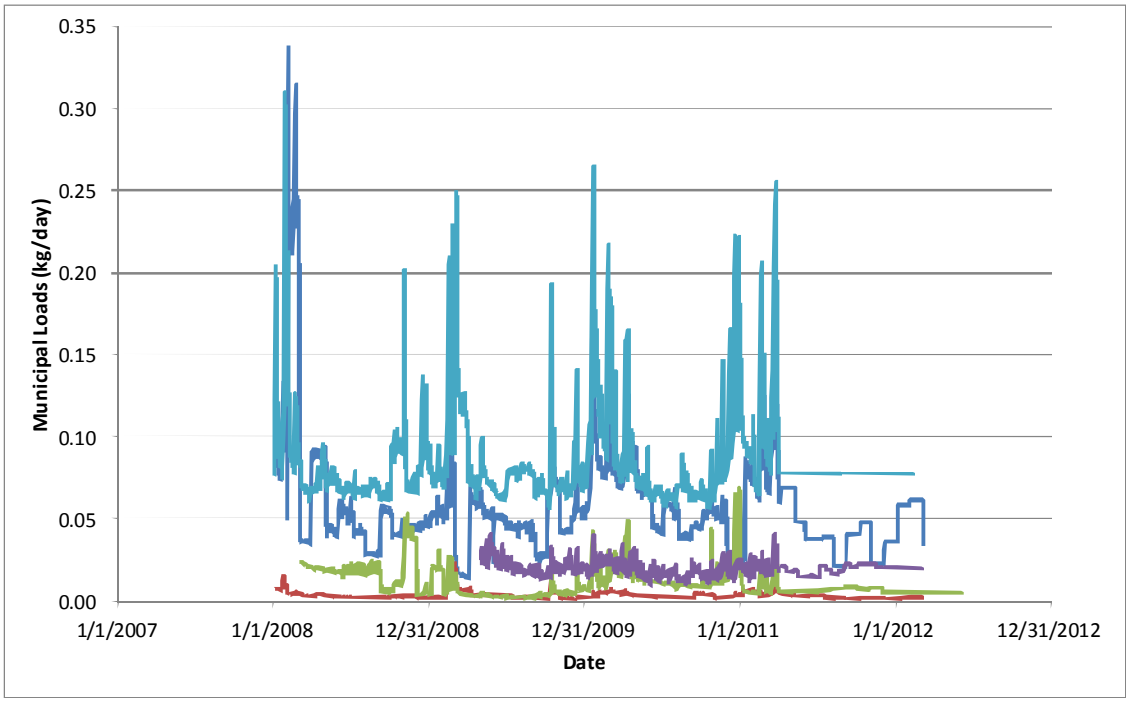

Figure 5-8
Example of daily total selenium loads from the major municipal dischargers for the period of 2008–2012.

5.6 Inputs from Tributaries

Inputs from ten tributaries were specified as flow multiplied by concentrations. Daily flow from Napa River was used to scale for tributaries without long-term flow records, based on modeled total runoff for each tributary (Davis, 2000). Dissolved and particulate selenium concentrations from the tributaries were sampled within this study during the March 2012 sampling event (Appendix f). These concentrations were used in the model inputs. Since particulate selenium species for the tributaries were also sampled, particulate selenium inputs from tributaries were added to the model. Total selenium concentrations sampled during this study were somewhat lower than values previously sampled within these watersheds as part of the SWAMP program (Figure 5-9).

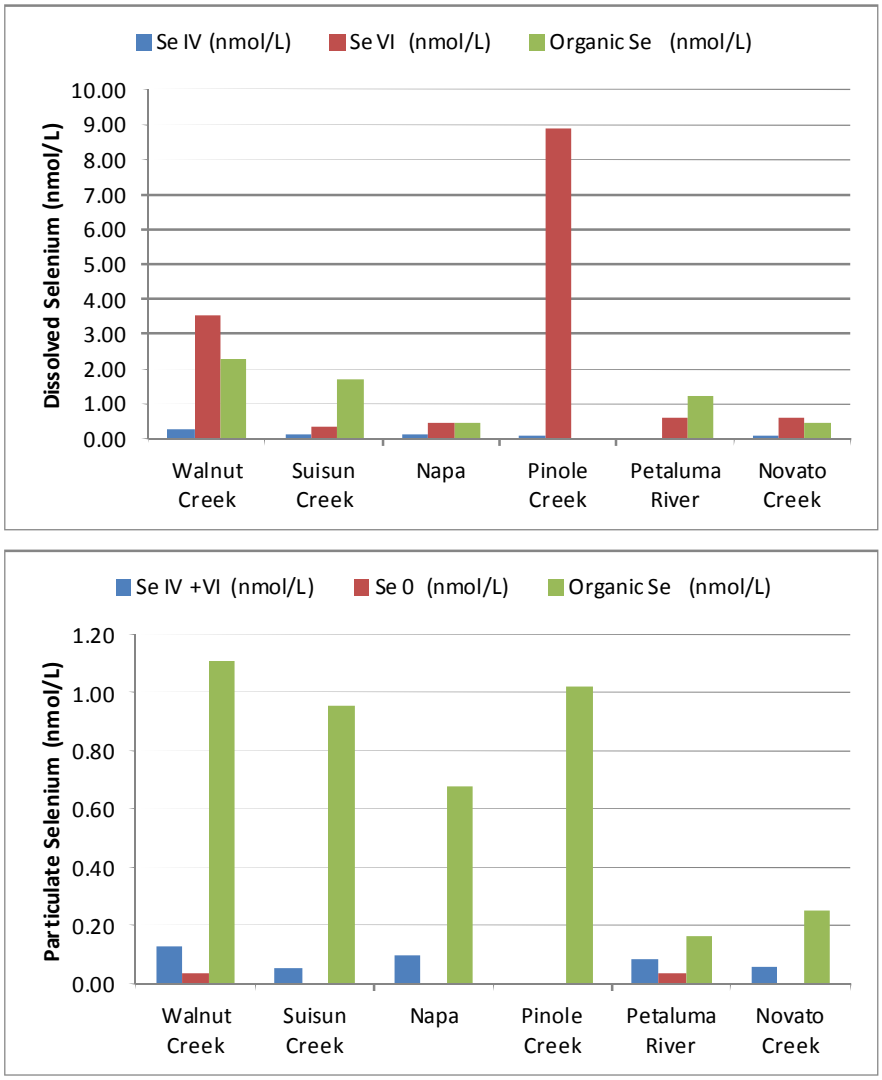

Figure 5-9
Dissolved and particulate selenium concentrations by species for six tributaries sampled during April 2012.

5.7 Modeling Approaches

Salinity

A change was made to the salinity modeling approach in the current update and resulted in improved salinity fits. Unlike the previous model, in which salinity and dissolved species were modeled using a constant, the salinity and dissolved species are now modeled using a dispersion coefficient derived from the following equation, by assuming steady-state for each time step:

$$0 = -U\frac{dS}{dx} + E\frac{d^2S}{dx_2} \quad (1)$$

Where S is salinity at distance x, U is velocity and E is the dispersion coefficient. E was estimated as a function of distance through this procedure.

TSM

Simulation of BEPS (Bed Exchangeable Particles) was recalibrated for the period of 2008–2012. The parameters for simulating velocity (a, b) and dispersion coefficient (c, d) of BEPS therefore changed from previous model.

The fraction of PSP (Permanently Suspended Particles) at Rio Vista was specified as 0.85, as in the previous model. The value was based on and equivalent to the fraction of suspended sediments with diameter less than <0.0625mm, which is expected to be largely in the suspended phase.

Selenium Transformations

The selenium transformation rates used in this updated model application mostly remained unchanged. Adjustments were made to the selenium uptake rates by phytoplankton uniformly by a factor of 1/10 to better match the simulated particulate organic selenide and total particulate selenium. It appears from recent sampling that uptake by phytoplankton may be overestimated using the rates used in Tetra Tech (2010).

Model Validation

The model was simulated for the entire time period from June 1998- April 2012. Model simulated results and the four transects sampled during this study for salinity, TSM, phytoplankton, dissolved and particulate selenium species were compared. The model simulated physical parameters including salinity, TSM, and phytoplankton were validated against the USGS monthly cruise data for the period of 2009–2012. Model simulated transects for the previous time periods (April 1999 and November) were also compared to transect data sampled by Cutter and Cutter (2004) and Doblin et al. (2005).

Model Evaluation Criteria

In addition to the previous model evaluation criteria used (r, correlation coefficient and goodness of fit, defined previously in Tetra Tech, 2010), several additional statistical measures were added to evaluate the quality of the model fit. These include:

MSE – The Mean Squared Error is a standard statistic that measures the bias between simulated and observed values. The optimal value is zero:

$$MSE = \left[\frac{\sum_{i=1}^{n} \left(Y_i^{Obs} - Y_i^{Sim} \right)^2}{n} \right] \quad (2)$$

RMSE – The Root Mean Squared Error is a standard statistic used to indicate accuracy of the simulation. It is the square root of the MSE. The optimal value is zero.

PBIAS – Percent bias measures the average tendency of the simulated data to be larger or smaller than the measured data. A value of 0 of optimal – a positive value indicates underestimation bias and a negative value indicate overestimation bias:

$$PBIAS = \left[\frac{\sum_{i=1}^{n} \left(Y_i^{Obs} - Y_i^{Sim} \right) * 100}{\sum_{i=1}^{n} \left(Y_i^{Obs} \right)} \right] \quad (3)$$

5.8 Modeling Results

Simulation for 2010 – 2012 Transects

Model-simulated physical parameters (salinity, TSM and chlorophyll a), dissolved selenium (selenite, selenate, and organic selenide) and particulate selenium (particulate selenite and selenate, particulate elemental, and particulate organic selenide) for the four sampling transects during 2010-2012 were compared to observed values (Figure 5-10 through Figure 5-25). In some cases, when data from transect sampling were missing, data from USGS bay cruise sampling from proximal sampling dates were used for comparison. Statistical measurements of model performance for each variable were also shown in Table 5-1 through Table 5-4.

The model simulated salinity for the four transects generally agreed with observed values. The 2010 dry season sampling showed a different pattern from the normal TSM profile existing in the bay and from the USGS sampling data, therefore this pattern in TSM was not captured by the model. The phytoplankton concentrations for fall 2010 sampling were lower than the USGS sampling data, however the model can be calibrated to the lower observed values (Figure 5-10).

For the 2010 dry season sampling, the dissolved selenium species generally showed a peak in the middle of the estuary, and this pattern was captured by the model (Figure 5-11). The particulate selenium species showed somewhat larger variations than the model predicted values, although in general the model predicted values are in the range of the observed values (Figure 5-12). This is likely due to local variations in sediment resuspension, which generates particulate elemental selenium, and is not captured by the model. Some local variations in particulate organic selenium that are not captured by the model, are most likely due to local variations in phytoplankton concentrations and species. The model simulated total particulate selenium (in µg/g) showed some over-predictions at higher salinities (Figure 5-13); this is mainly due to increases in phytoplankton and associated selenium uptake toward Golden Gate, and the mismatch in TSM profile.

The model performance for 2010 dry season transect measured by the goodness of fit (GOF) is relatively high, generally greater than 85% for salinity and dissolved selenium species (Table 5-1). The percent bias (PBIAS) is generally less than 15%. Phytoplankton and particulate selenium species, due to some local variations not captured by the model, generally showed larger percent bias and lower goodness of fit.

The spring 2011 sampling showed an increase in TSM toward Golden Gate (Figure 5-14). This pattern is somewhat captured by the model. The model is able to predict a similar estuarine turbidity maximum (ETM), although at an upper estuary location. The phytoplankton concentrations for the spring 2011 sampling showed elevated levels at the head of estuary and the lower estuary. Due to lower temperature and solar radiation, the simulated phytoplankton is generally low during March and therefore the bloom event was not captured by the model.

For the spring 2011 sampling, the dissolved selenium species generally showed a more conservative behavior in the estuary, and this pattern is well captured by the model (Figure 5-15).

The GOF greater than 92% for dissolved selenium species (Table 5-2). The particulate selenium species generally are predicted well by the model (Figure 5-16). The particulate elemental selenium generally showed low concentrations (non-detect) during this high flow sampling event. This species is slightly over-predicted by the model. In general, total particulate selenium (in µg/g) is predicted well by the model, except the high values associated with phytoplankton bloom at the head of estuary (Figure 5-17), with GOF of 50%.

The model performance for the spring 2011 transect measured by GOF is relatively high, with GOF values generally greater than 75% for salinity and dissolved selenium species (Table 5-2). The percent bias (PBIAS) is generally less than 15%. Phytoplankton and particulate selenium species, due to some local variations not captured by the model, generally showed larger percent bias and lower goodness of fit.

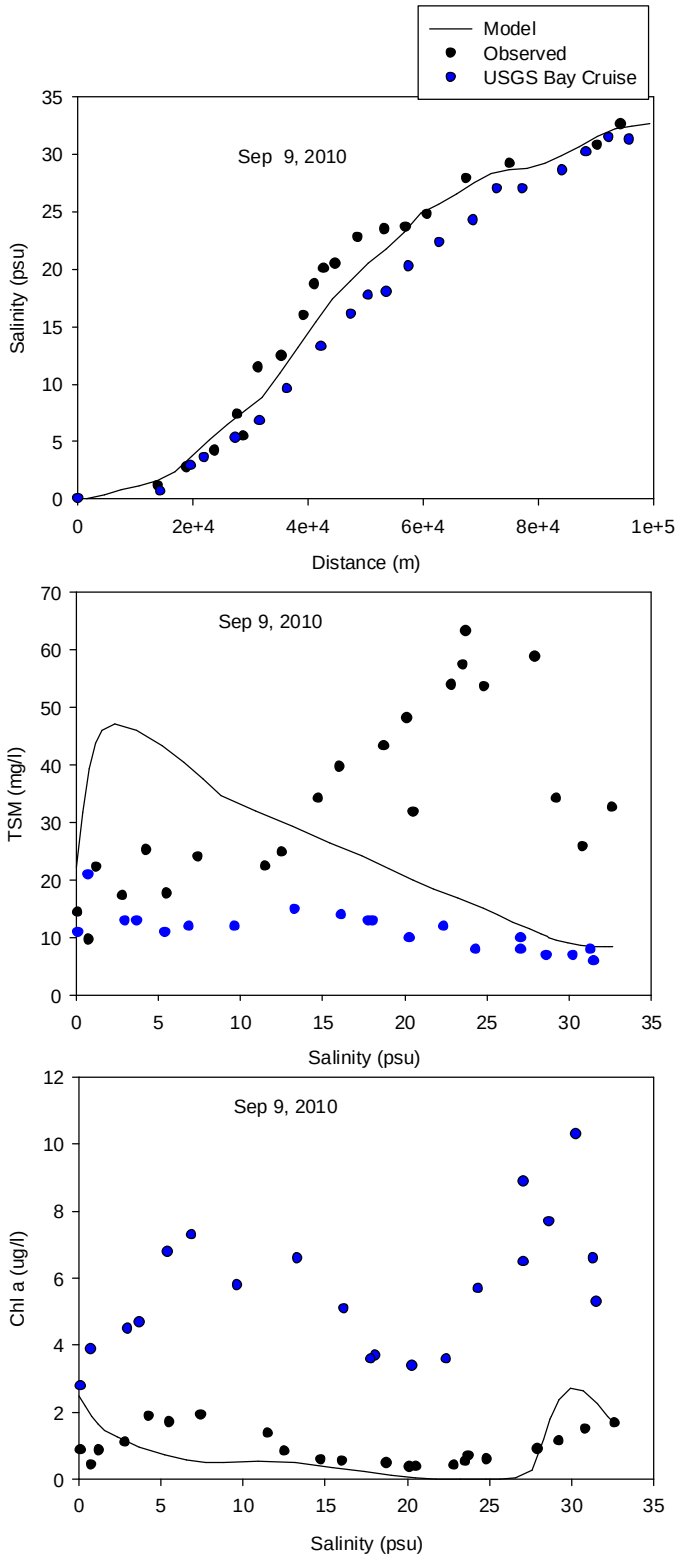

Figure 5-10
Model simulated salinity, TSM, and Chlorophyll a compared to observed values for the 2010 dry season transect.

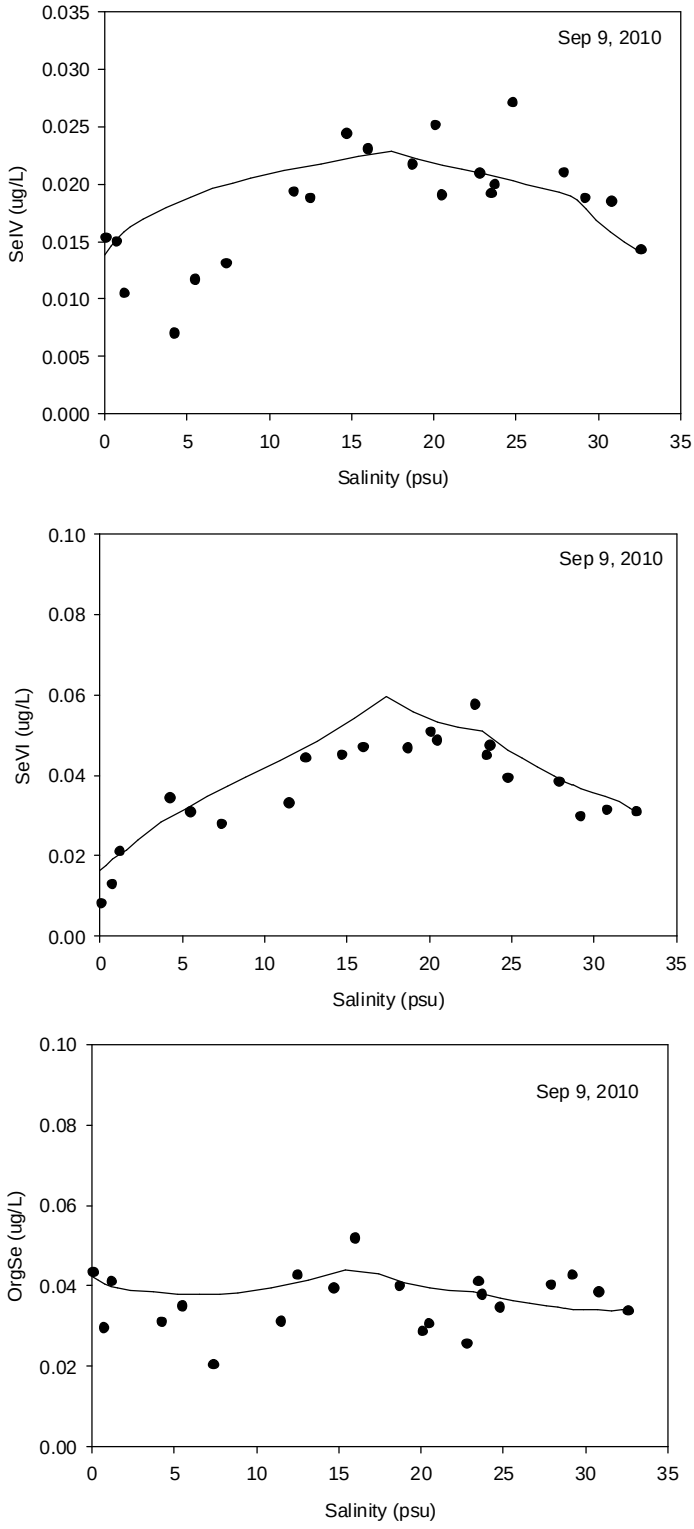

Figure 5-11
Model simulated selenite, selenate and organic selenide compared to observed values for the 2010 dry season transect.

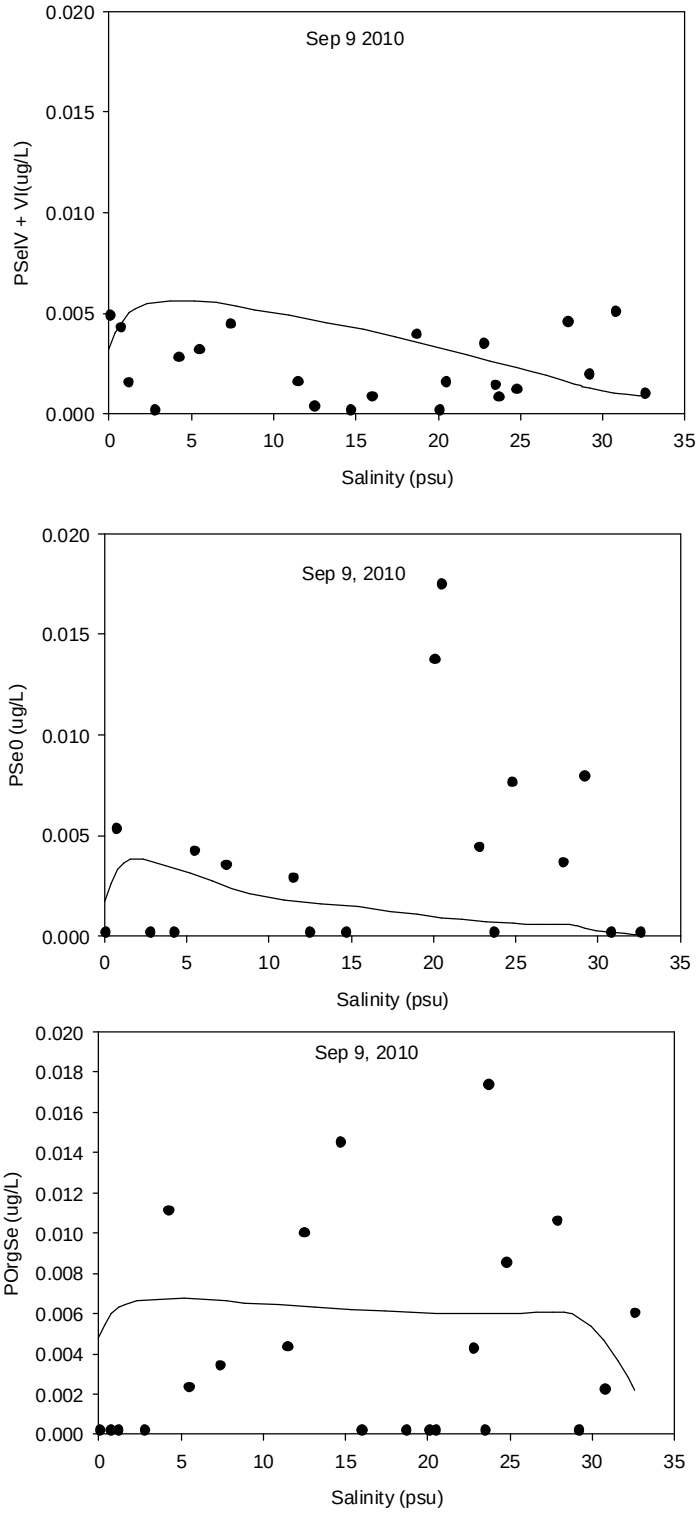

Figure 5-12
Model simulated particulate selenite and selenate, particulate elemental selenium, and particulate organic selenium compared to observed values for the 2010 dry season transect.

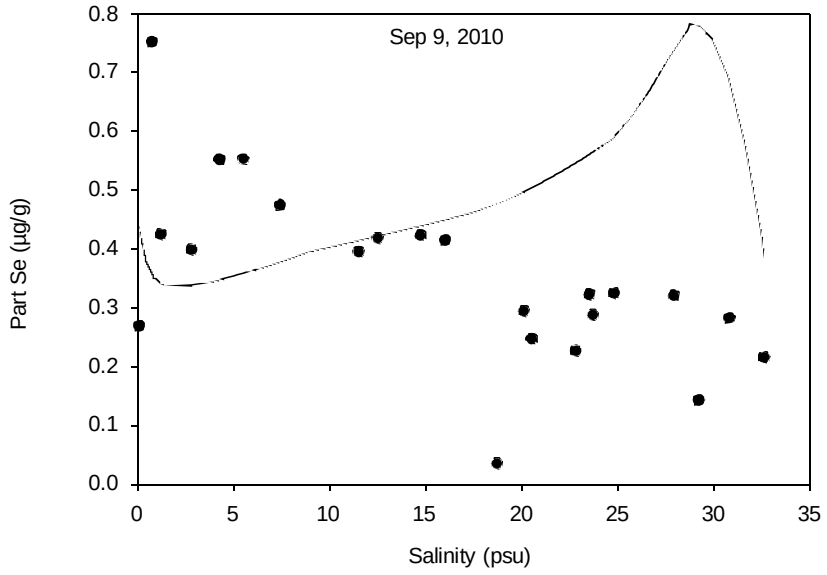

Figure 5-13
Model simulated particulate selenium (in µg/g) compared to observed values for the 2010 dry season transect.

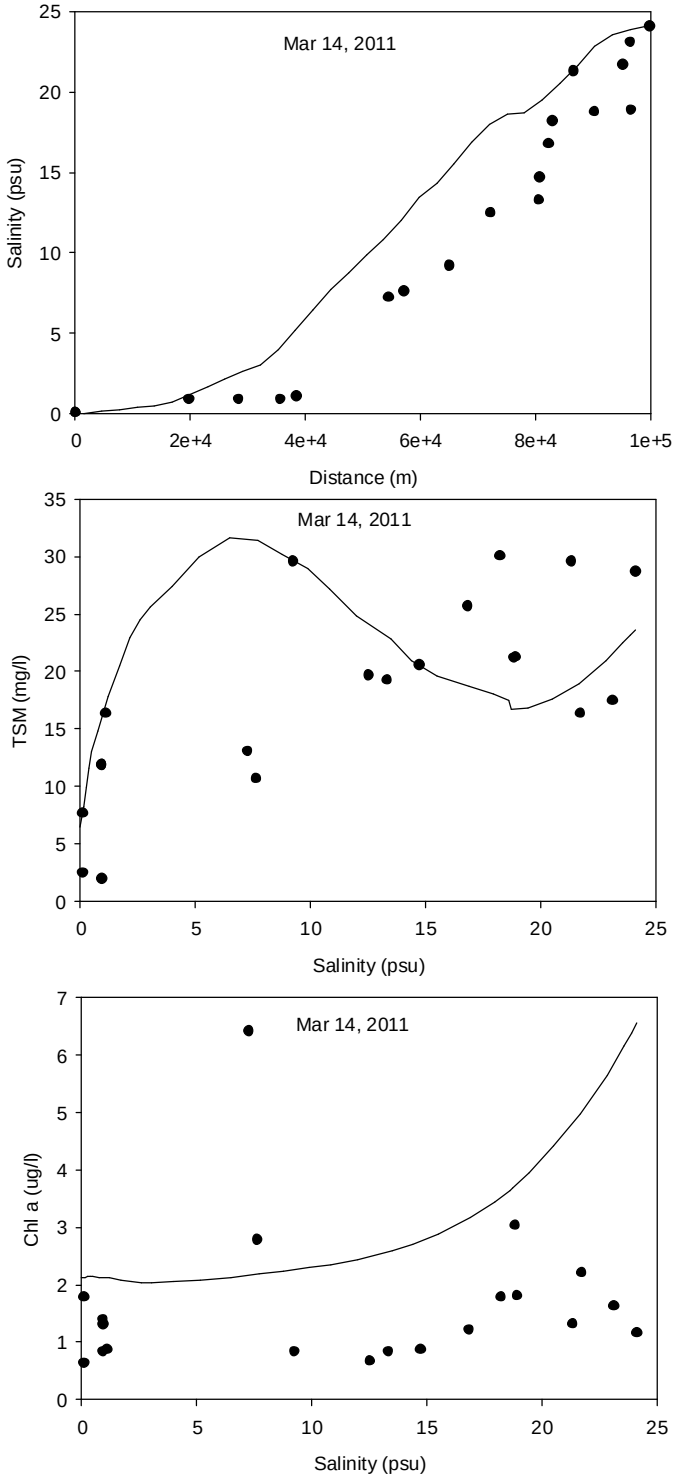

Figure 5-14
Model simulated salinity, TSM, and Chlorophyll a compared to observed values for the spring 2011 transect.

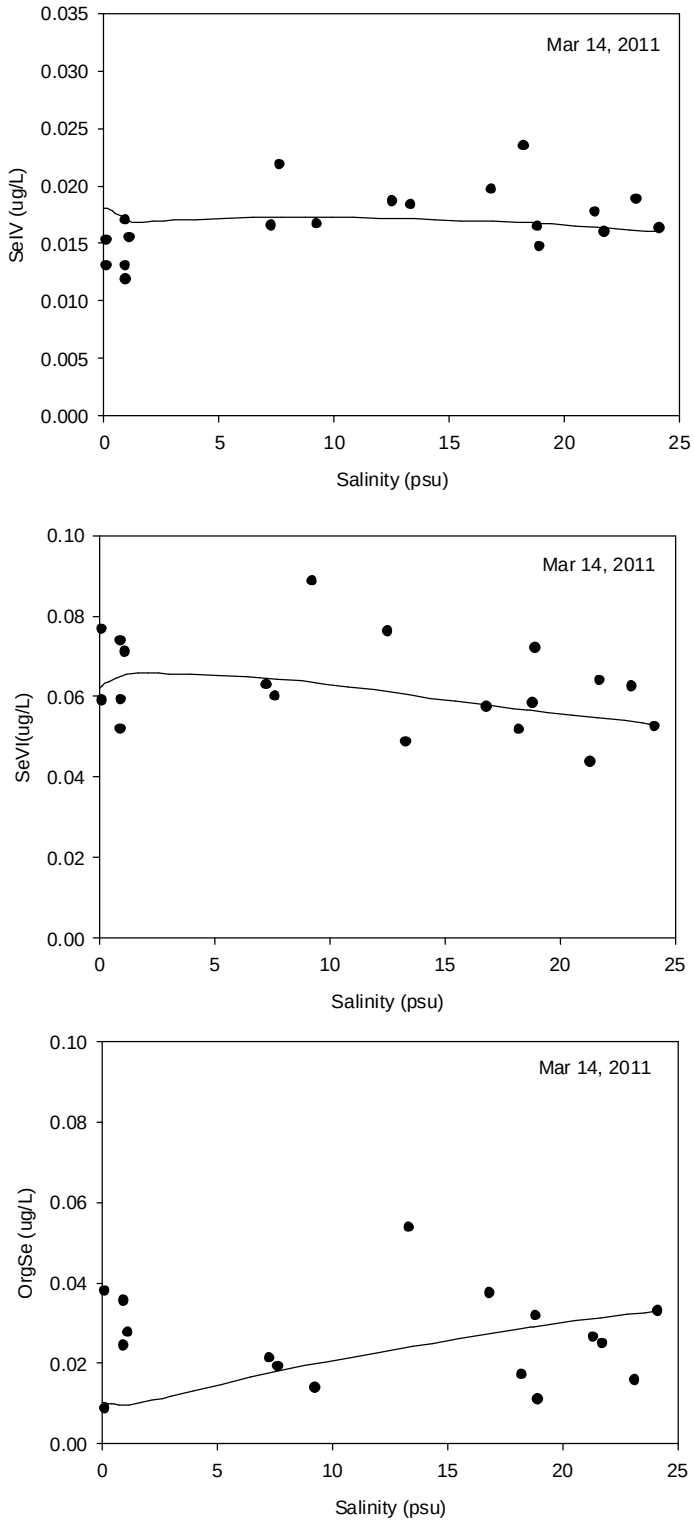

Figure 5-15
Model simulated selenite, selenate and organic selenide compared to observed values for the spring 2011 transect.

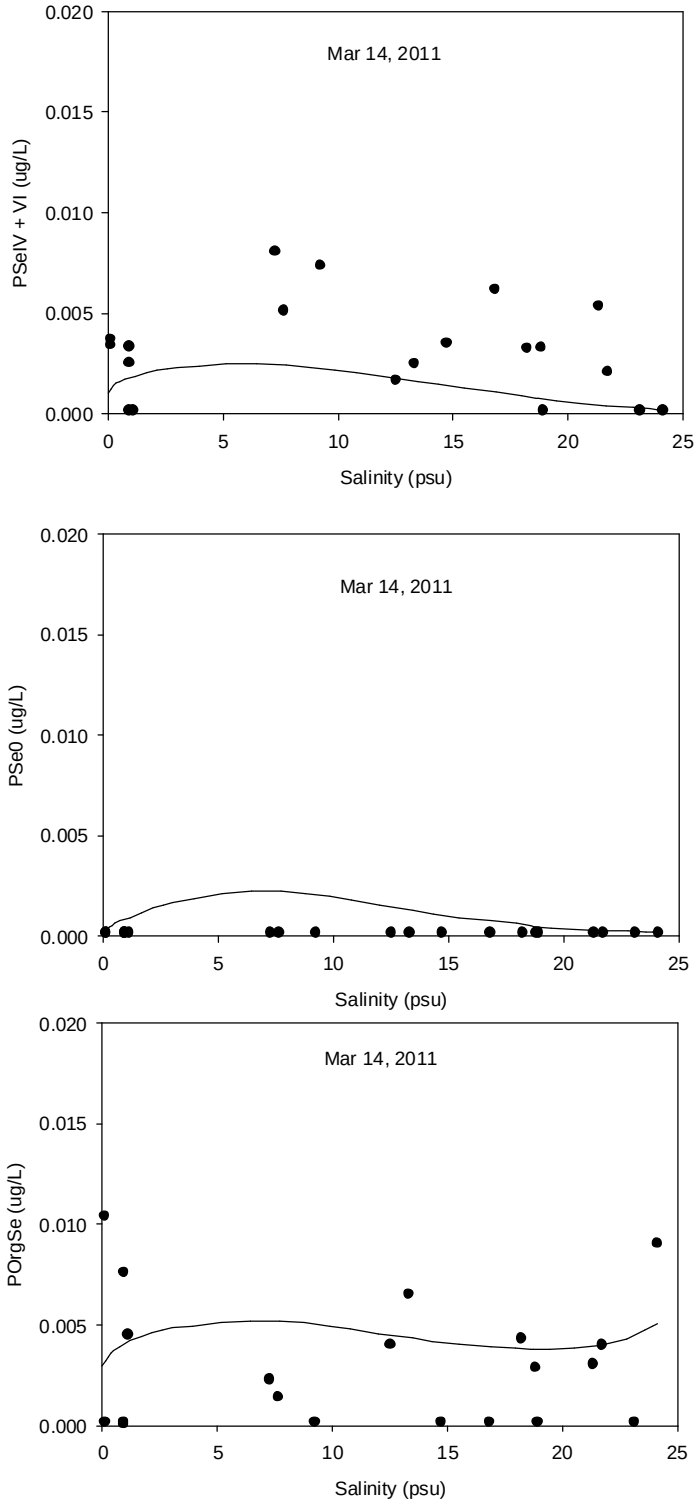

Figure 5-16
Model simulated particulate selenite and selenate, particulate elemental selenium, and particulate organic selenium compared to observed values in the spring 2011 transect.

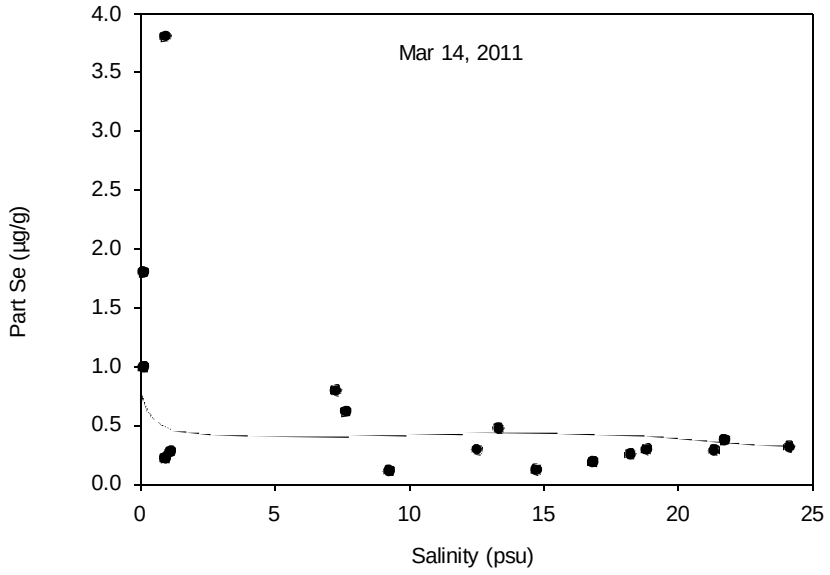

Figure 5-17
Model simulated particulate selenium (in µg/g) compared to observed values for the spring 2011 transect.

The October 2011 dry season sampling showed very good agreement of model simulated salinity with observed values (NSE =0.999 and GOF = 93.47%) and with observed values for TSM (NSE = 0.969 and GOF =94.85%; Figure 5-18). The model is able to capture the location and magnitude of the estuary turbidity maximum exhibited in this profile. Observed phytoplankton concentrations are missing from this sampling event, therefore data from USGS bay cruise sampling for the nearby dates were used for comparison. The model is generally able to capture the trend on phytoplankton exhibited in the estuary near the fall 2011 sampling event.

The predicted dissolved selenium species generally agreed with the observed values (NSE =0.930-0.948; GOF = 79.2-87%; Figure 5-19). Some slight under-predictions were seen for selenite and selenate. This could be due to uncertainties in speciation of refineries and other local dischargers, as the refinery effluent speciation sampling only extends to August, 2011 and values from the last sampling (08/2011) were used for the rest of the simulation period. Particulate selenium species were simulated well by the model (NSE = 0.922 - 9.62; GOF = 79.87 - 98.97%; Figure 5-20). Simulated particulate selenium (in µg/g) is able to mimic the pattern exhibited in the estuary transect, with higher concentrations at the head of the estuary, decreases in particulate selenium up to salinity 2.5 and further increases in particulate selenium towards the Golden Gate (Figure 5-21).

The model performance for the 2011 dry season was considered the best among the four transects, as measured by various criteria (Table 5-3). The NSE values are greater than 0.85 for all species simulated (including TSM, dissolved and particulate selenium species). The GOF is greater than 79% for all species simulated. Percent bias is less than 20% for all species except for particulate organic selenium.

For the spring 2012 sampling, simulated salinity showed slight over-predictions (Figure 5-22). The model is able to capture the location of the ETM, however, it under-predicted its magnitude. The agreement for simulated and observed phytoplankton is high. The dissolved selenium species from spring 2012 are also generally predicted well by the model (NSE = 0.90-0.97; GOF = 01.37 – 96.90; Figure 5-23). The model is able to predict the relatively conservative behavior of

selenate and some slight peaks in the middle of the estuary, the general decreasing trend in organic selenide and the generally increasing trend in selenite. The selenite calculations showed some under-predictions in peaks in estuary. This could also be related to uncertainties in refinery speciation and speciation from other local dischargers. The particulate selenium species are generally predicted well by the model (NSE=0.499 - 0.952; Figure 5-24). The particulate elemental selenium concentrations during this high flow sampling event are low (mostly at non-detect levels) and were slightly over-predicted by the model. The model simulated particulate selenium (in µg/g) showed some slight over-prediction (Figure 5-25) due to two factors: 1) under-prediction in ETM, and 2) some over-predictions in elemental selenium.

The model performance for spring 2012 transect measured by Nash-Sutcliffe coefficient (NSE) is relatively high, with NSE values generally greater than 0.82 for all species except PSe0 (

Table 5-4). The percent bias (PBIAS) is generally less than 15%, and the goodness of fit (GOF) usually greater than 85% for salinity and dissolved selenium species. Particulate selenium species, due to local variations not captured by the model, generally showed larger percent bias and lower goodness of fit. Overall the fit for particulate selenium (in µg/g) is still relatively good (NSE =0.822 and GOF = 83.12%), and for PSeIV+VI (NSE = 0.952 and GOF = 88.01%).

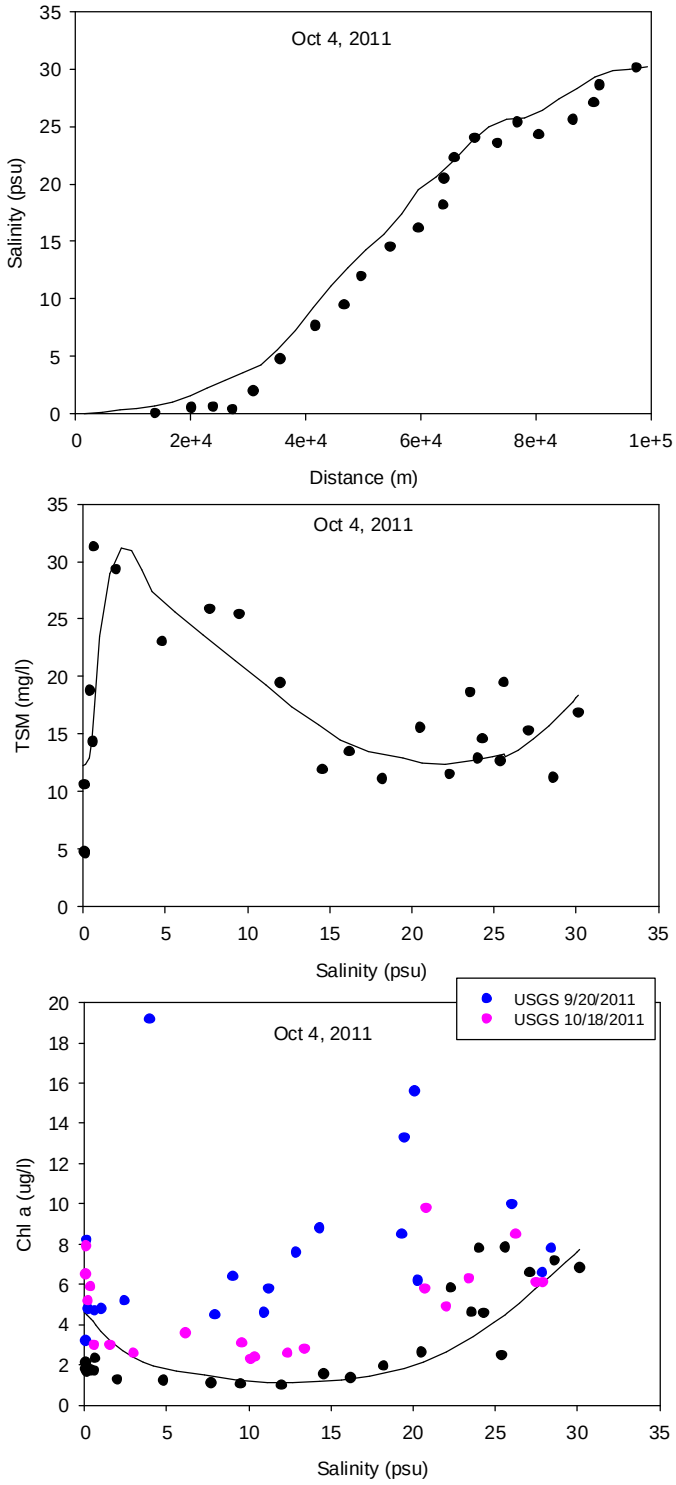

Figure 5-18
Model simulated salinity, TSM, and Chlorophyll a compared to observed values for the 2011 dry season transect.

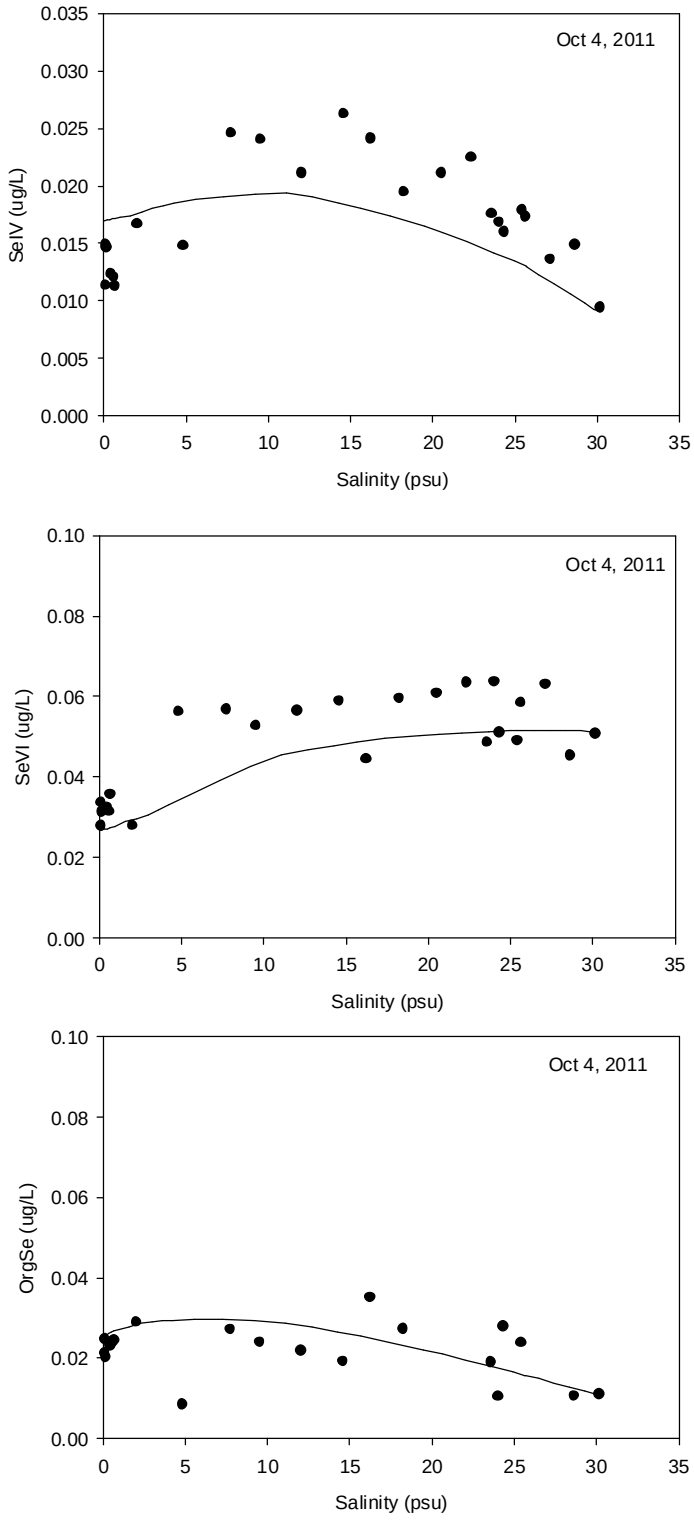

Figure 5-19
Model simulated selenite, selenate and organic selenide compared to observed values for the 2011 dry season transect.

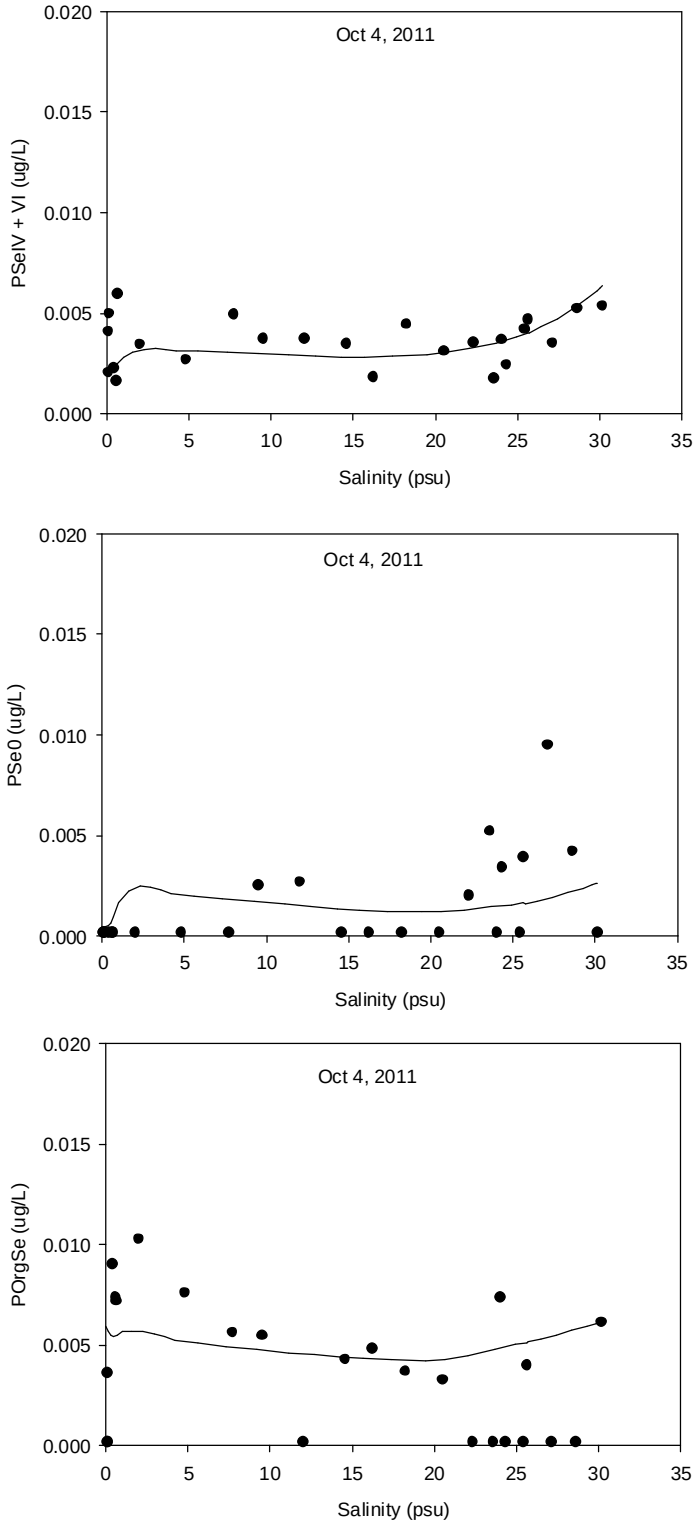

Figure 5-20
Model simulated particulate selenite and selenate, particulate elemental selenium, and particulate organic selenium compared to observed values for the 2011 dry season transect.

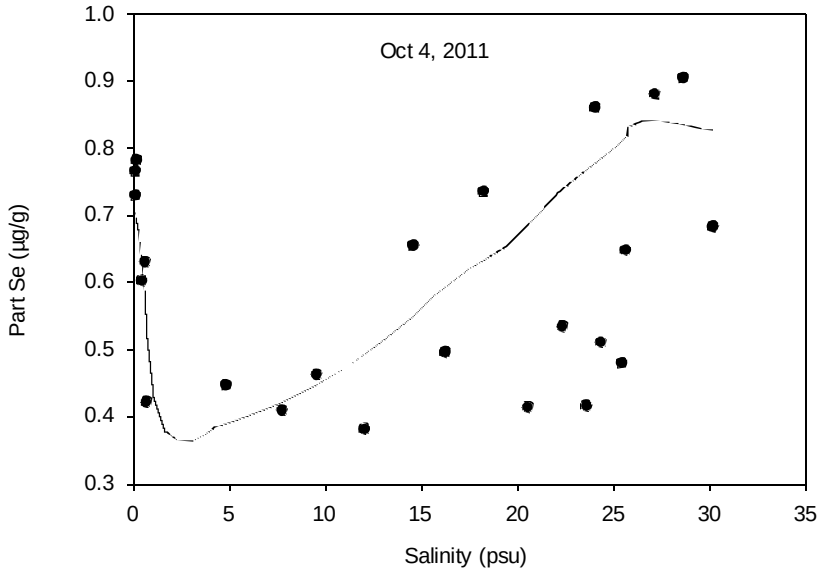

Figure 5-21
Model simulated particulate selenium (in µg/g) compared to observed values for the 2011 dry season transect.

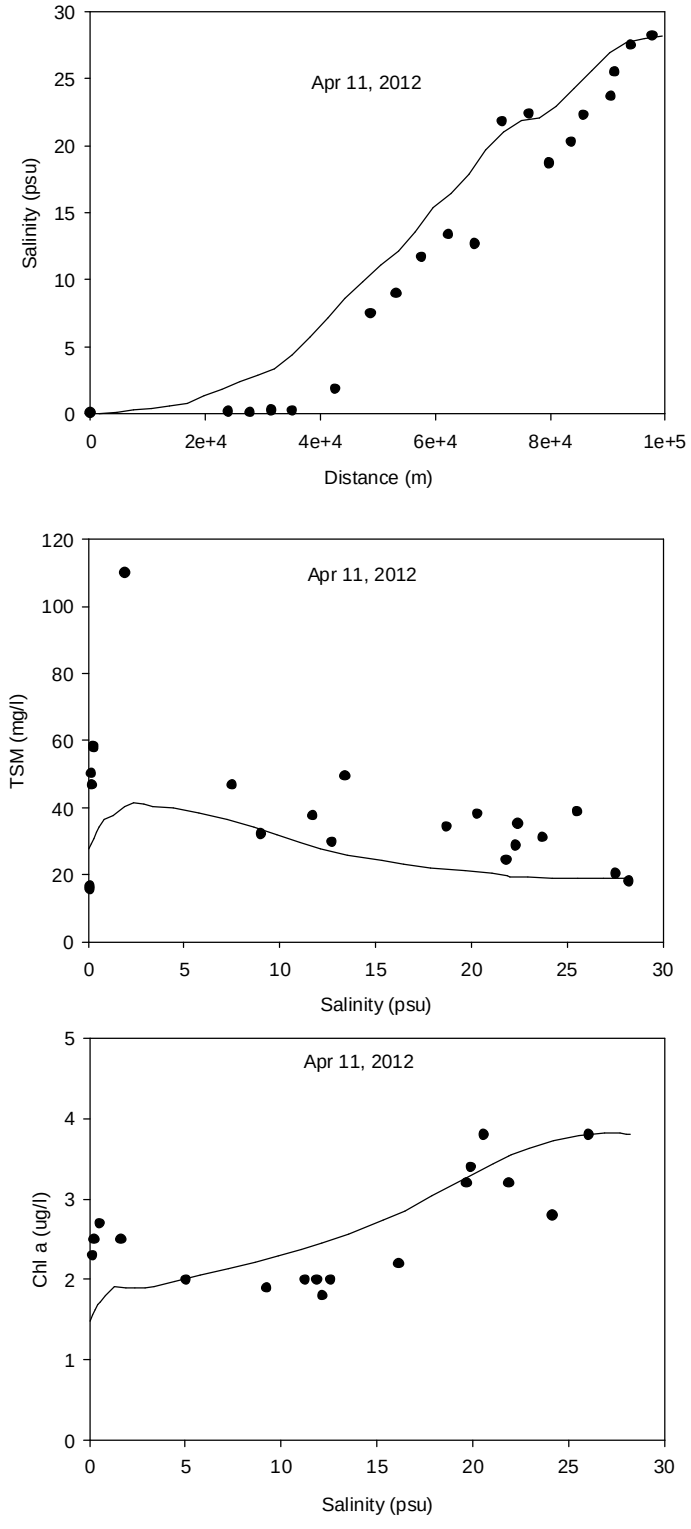

Figure 5-22
Model simulated salinity, TSM, and Chlorophyll a compared to observed values for the spring 2012 transect.

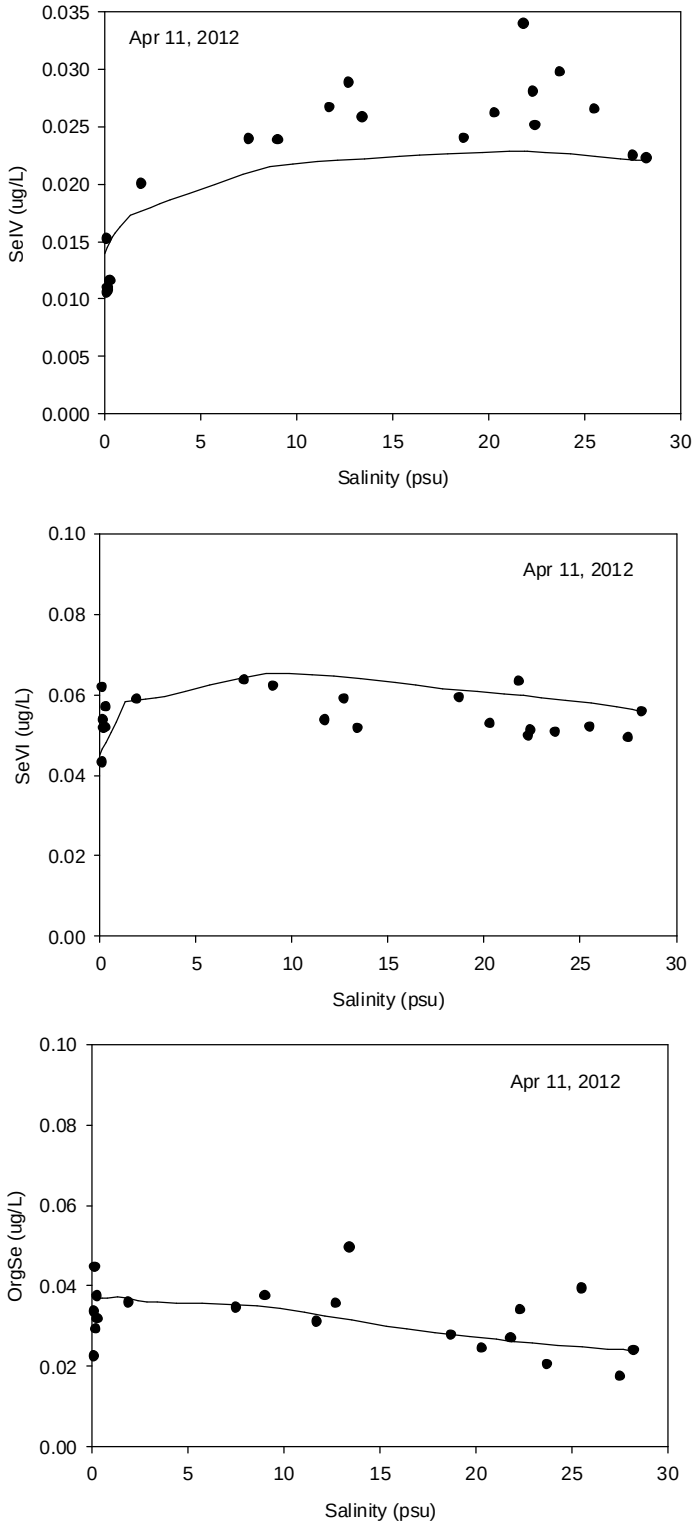

Figure 5-23
Model simulated selenite, selenate and organic selenide compared to observed values for the spring 2012 transect.

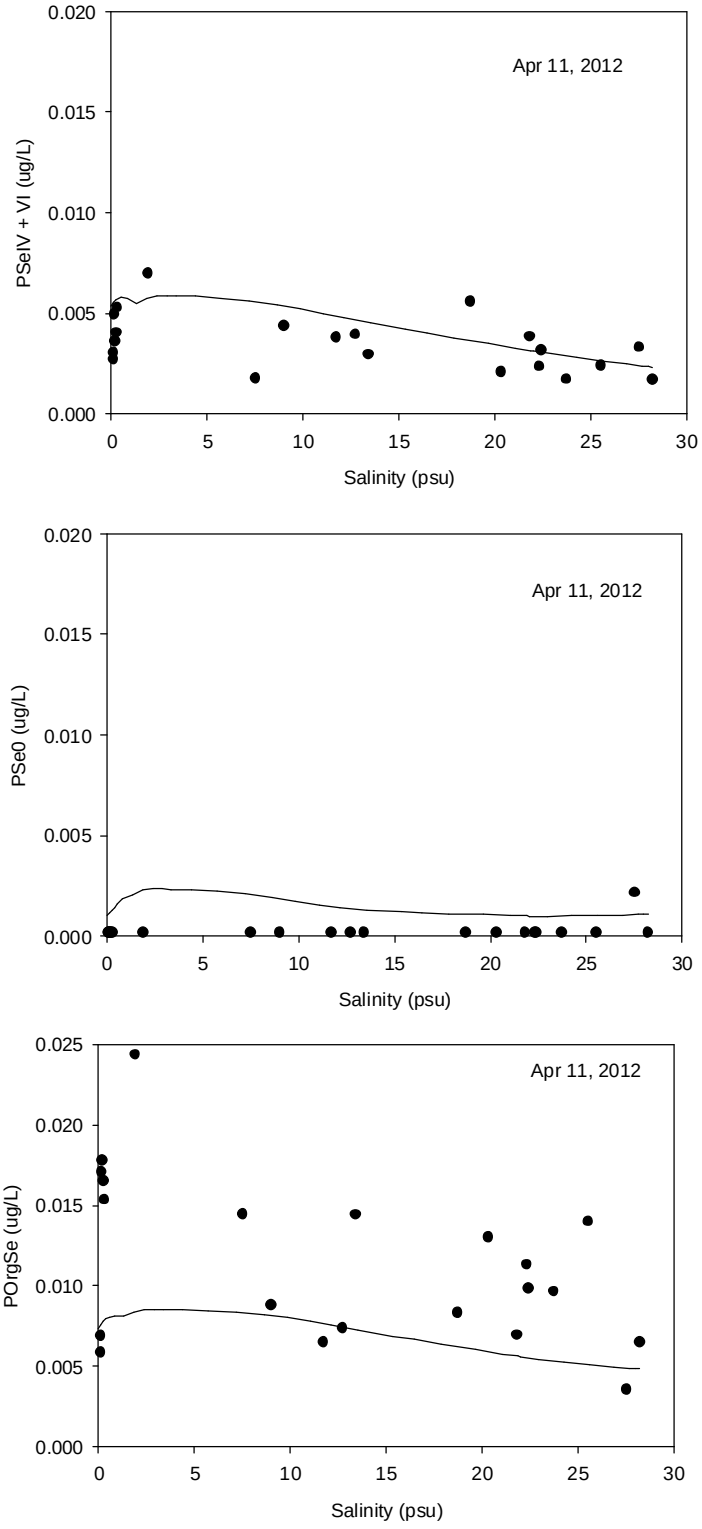

Figure 5-24
Model simulated particulate selenite and selenate, particulate elemental selenium, and particulate organic selenium compared to observed values compared to the spring 2012 transect.

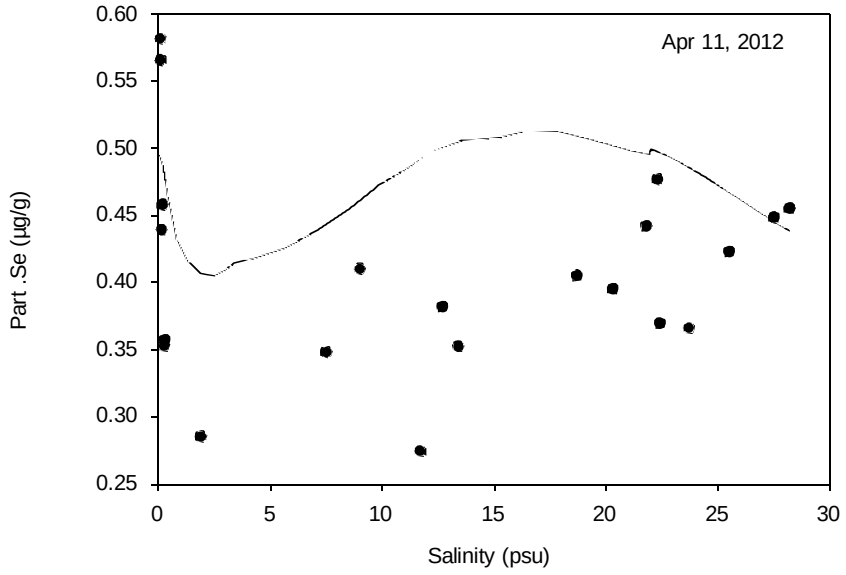

Figure 5-25
Model simulated total particulate Se values compared to spring 2012 transect observations.

Table 5-1
Statistical Measures for Goodness of Fit for Simulations of the September 2010 Transect

		Field salinity (psu)	Lab salinity (psu)	SeIV (µg/l)	SeVI (µg/l)	Total Dis. Se (µg/l)	Org Se (µg/l)	Chla (µg/l)	TSM (mg/l)	Total Part. Se (µg/l)	PSeIV + VI (µg/l)	PSe0 (µg/l)	POrg Se (µg/l)	Part Se (µg/g)
MSE	optimal 0	6.13	6.03	0.00	0.00	0.00	0.00	0.46	704.00	0.00	0.00	0.00	0.00	0.06
RMSE	optimal 0	2.476	2.455	0.006	0.007	0.022	0.012	0.677	26.533	0.006	0.003	0.012	0.005	0.253
PBIAS	optimal 0	-8.723	-7.998	13.543	11.981	12.7	13.1	-30.2	-26.9	0.445	76.200	-81.1	39.169	40.985
GOF(%)		90.87	92.18	87.29	88.68	88.00	87.69	63.87	68.56	99.56	42.59	-86.58	66.80	65.48
r		0.980	0.977	0.513	0.934	0.746	-0.102	0.513	-0.608	-0.040	-0.141	0.059	-0.041	-0.547

Table 5-2
Statistical Measures for Goodness of Fit for Simulations of the March 2011 Transect

		Field salinity (psu)	Lab salinity (psu)	SeIV (µg/l)	SeVI (µg/l)	Total Dis. Se (µg/l)	Org Se (µg/l)	Chla (µg/l)	TSM (mg/l)	Total Part. Se (µg/l)	PSeIV + VI (µg/l)	PSe0 (µg/l)	POrg Se (µg/l)	Part Se (µg/g)
MSE	optimal 0	11.44	15.60	0.00	0.0001	0.0001	0.0002	92.24	108.49	0.00	0.00	0.00	0.00	0.71
RMSE	optimal 0	3.383	3.950	0.003	0.012	0.010	0.014	9.604	10.416	0.003	0.003	0.001	0.003	0.840
PBIAS	optimal 0	21.323	15.248	-3.203	-6.082	-2.815	7.754	-60.424	10.399	15.253	-64.675		52.689	-38.672
GOF(%)		80.64	78.35	96.74	93.72	97.14	92.72	3.95	90.10	85.79	-8.82		57.36	50.62
r		0.968	0.923	0.024	0.222	0.177	0.126	-0.044	-0.474	-0.061	0.158		0.243	0.159

Table 5-3
Statistical Measures for Goodness of Fit for Simulations of the October 2011 Transect

		Field salinity (psu)	Lab salinity (psu)	SeIV (µg/l)	SeVI (µg/l)	Total Dis. Se (µg/l)	Org Se (µg/l)	Chla (µg/l)	TSM (mg/l)	Total Part. Se (µg/l)	PSeIV + VI (µg/l)	PSe0 (µg/l)	POrg Se (µg/l)	Part Se (µg/g)
MSE	optimal 0	1.54	1.21	0.00	0.00	0.00	0.00		26.42	0.00	0.00	0.00	0.00	0.09
RMSE	optimal 0	1.242	1.098	0.006	0.012	0.021	0.012		5.140	0.002	0.002	0.002	0.003	0.295
PBIAS	optimal 0	6.688	2.881	-18.898	-16.558	-11.239	11.556		2.827	5.788	-9.859	5.533	21.818	-1.513
GOF(%)		93.47	95.05	86.98	88.15	95.60	79.17		94.85	91.15	98.97	93.58	79.87	89.50
r		0.997	0.994	0.425	0.776	0.881	0.502		0.663	0.561	0.373	0.133	0.162	0.408

Table 5-4
Statistical Measures for Goodness of Fit for Simulations of the April 2012 Transect

		Field salinity (psu)	Lab salinity (psu)	SeIV (µg/l)	SeVI (µg/l)	Total Dis. Se (µg/l)	Org Se (µg/l)	Chla (µg/l)	TSM (mg/l)	Total Part. Se (µg/l)	PSeIV + VI (µg/l)	PSe0 (µg/l)	POrg Se (µg/l)	Part Se (µg/g)
MSE	optimal 0	7.09	6.75	0.0000	0.0000	0.0001	0.0001		457.10	2.6771 E-05	1.7823 E-06	1.9099 E-06	0.0000	0.01
RMSE	optimal 0	2.664	2.599	0.005	0.006	0.009	0.007		21.380	0.005	0.001	0.001	0.007	0.101
PBIAS	optimal 0	14.229	14.118	-6.012	9.005	0.680	-7.551		-35.712	-22.095	12.728	379.346	-44.173	18.361
GOF(%)		86.69	86.78	93.80	91.37	99.32	96.90		55.46	74.97	88.01	-73.27	40.88	83.12
r		0.986	0.971	0.929	0.608	0.432	0.503		0.66	0.73	0.58	-0.17	0.65	-0.18

Validation for the 1999 Transects

The model with updated inputs of refinery, tributary and local dischargers, boundary conditions, selenium uptake rates, updated salinity formula and TSM calibration, was also validated for the 1999 sampling transects, using the same approach as used for the more recent observations.

For the April 1999 transect, model simulated physical parameters agreed well with the model (GOF= 68.6 – 84.9%; Figure 5-26). The model is able to capture the location and magnitude of the ETM for the April 1999 transect, which is considered as an improvement over the previous modeling result. Dissolved selenium species showed very similar patterns to the previous results (GOF = 67.6-92.6%; Figure 5-27; Tetra Tech, 2010). The organic selenide seems slightly under-predicted. There are some local variations in organic selenide that is not captured by the model. This could be due to the speciation of refineries (values sampled in October 1999) and tributaries (values sampled in March 2012) assumed in the model. Particulate selenium species showed similar patterns to previous results, but generally with better agreement of spatial pattern (i.e. location and magnitude of estuary peaks; Figure 5-28; GOF = 48.08-77.66%). The particulate organic selenide showed some over-prediction. This indicates dissolution (mineralization) of particulate organic selenide to dissolved organic selenide may be possibly underestimated. Model simulated particulate selenium (in µg/g) showed very good agreement with observed values for April 1999 transect, capturing the general spatial pattern observed in particulate selenium (Figure 5-29). Model performance evaluation for April 1999 is shown in Table 5-5.

The November 1999 simulation showed results similar to previous modeling, with good agreement for salinity, and some over-prediction in TSM (GOF = 75.88 – 95.5%; Figure 5-30). The agreement for simulated and observed chlorophyll a concentrations is high (GOF = 86.62%). With the updated inputs of selenium from refineries, tributaries and local dischargers and better speciation data, the model is able to better capture the estuary peaks in dissolved selenium species, particularly for selenate and organic selenide (GOF = 75.17 – 94.5%; Figure 5-31). The model seems to over-predict selenite in the middle of the estuary. Again this could be due to uncertainties in speciation of inputs from various dischargers. The model simulated particulate selenium species seem to agree better with observed values, compared to previous simulation (GOF = 49.67% - 98.98%; Tetra Tech, 2010), particularly for particulate elemental selenium (Figure 5-32). Simulated particulate selenium (in µg/g) showed similar results to previous modeling (GOF = 91.13%; Figure 5-33), with some under-prediction in head of estuary due to over-prediction in TSM. This suggests that a TSM calibration that works for one condition (e.g., October 2011 may not work as well for other conditions). Model performance evaluation for November 1999 is shown in Table 5-6.

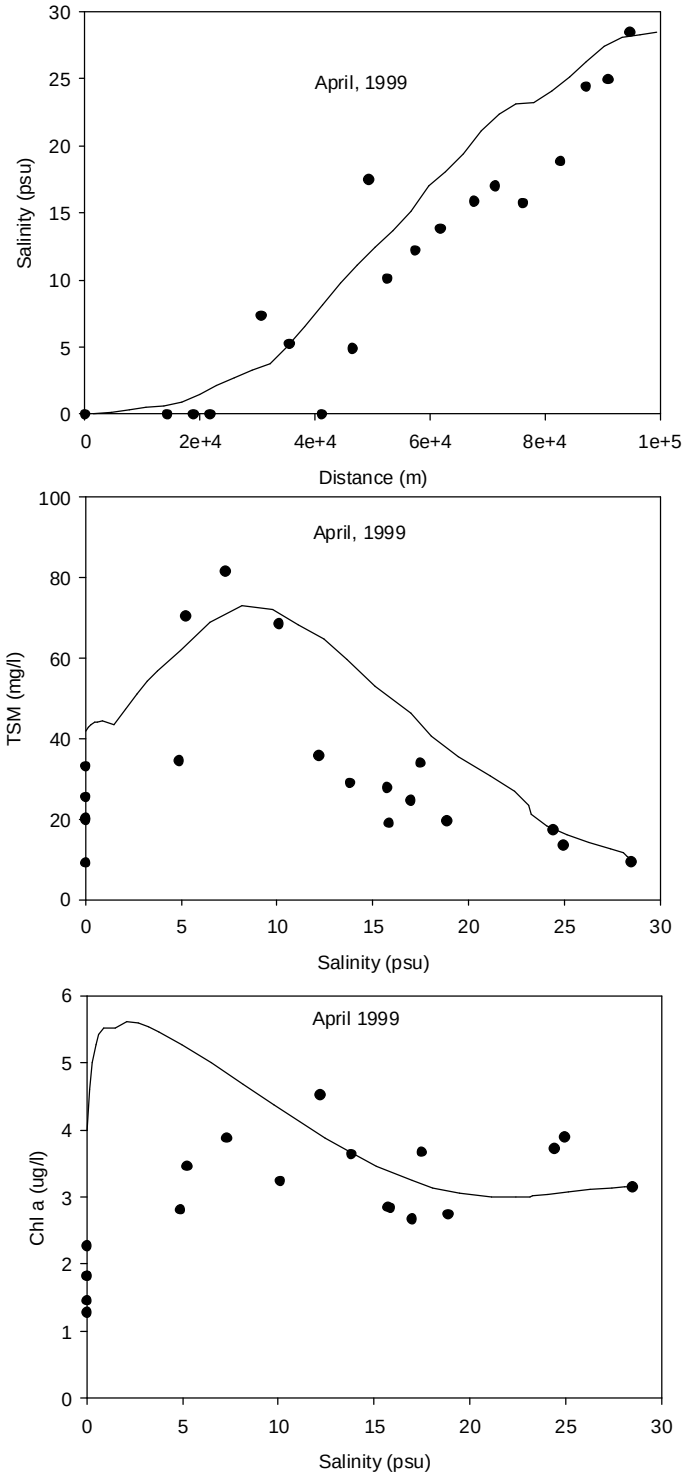

Figure 5-26
Model simulated salinity, TSM, and Chlorophyll a compared to observed values for the April 1999 transect.

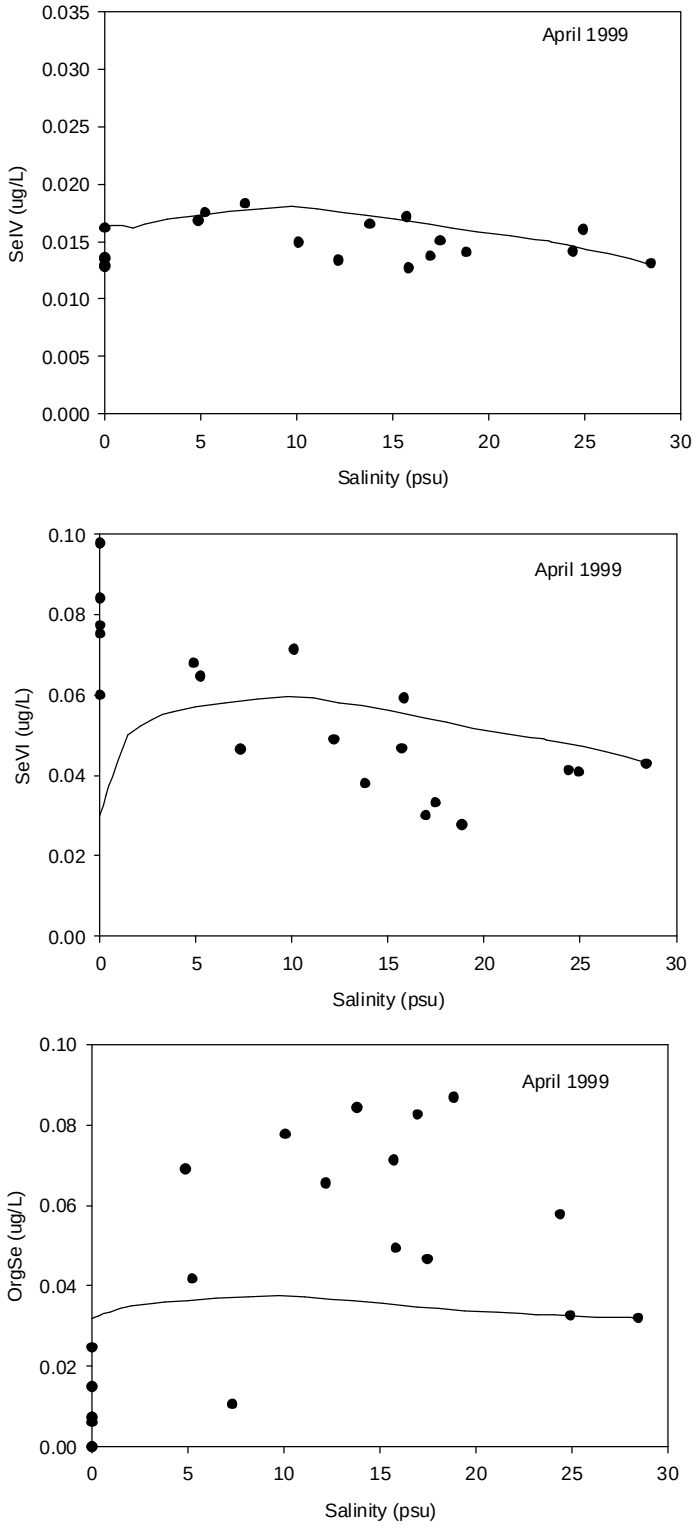

Figure 5-27
Model simulated selenite, selenate and organic selenide compared to observed values for the April 1999 transect.

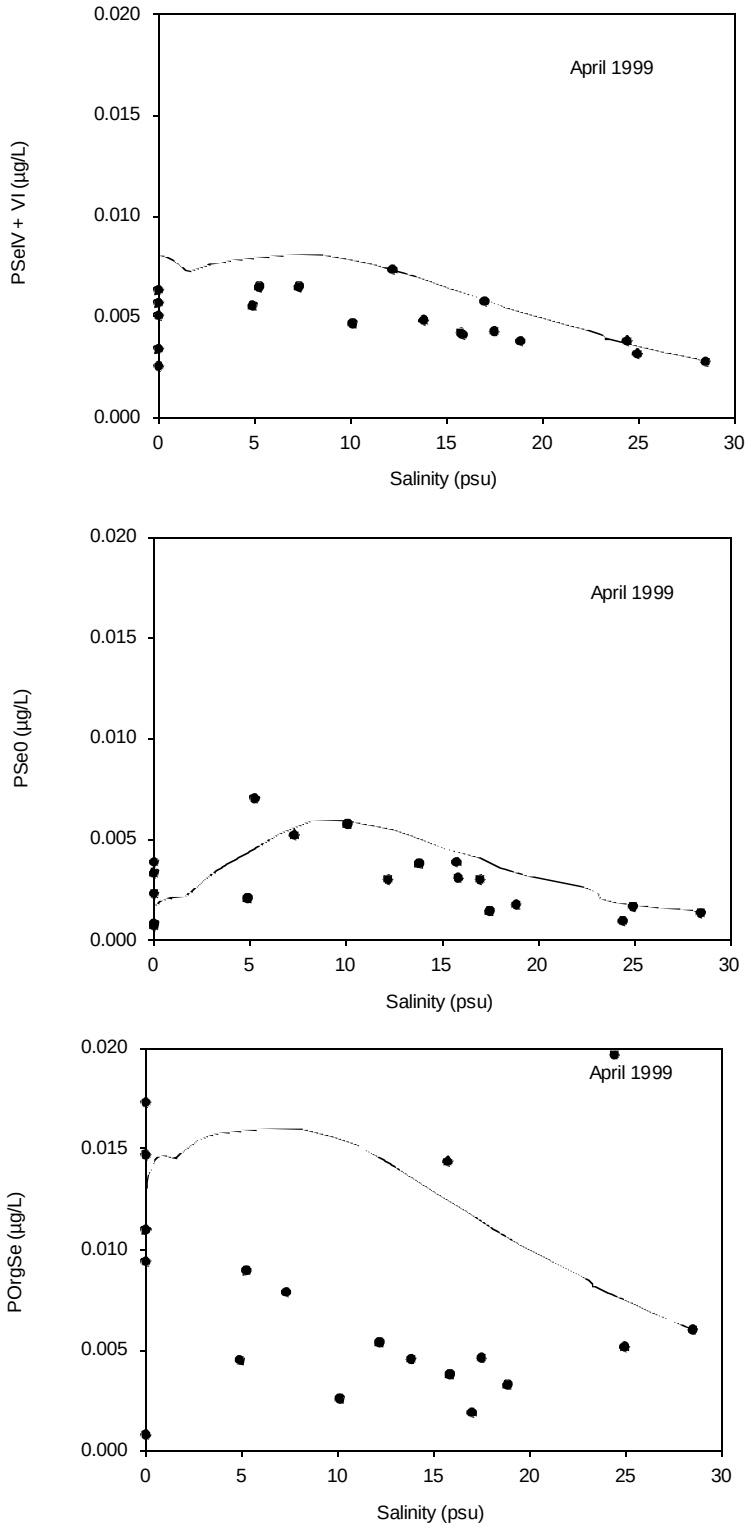

Figure 5-28
Model simulated particulate selenite and selenate, particulate elemental selenium, and particulate organic selenium compared to observed values compared to the April 1999 transect.

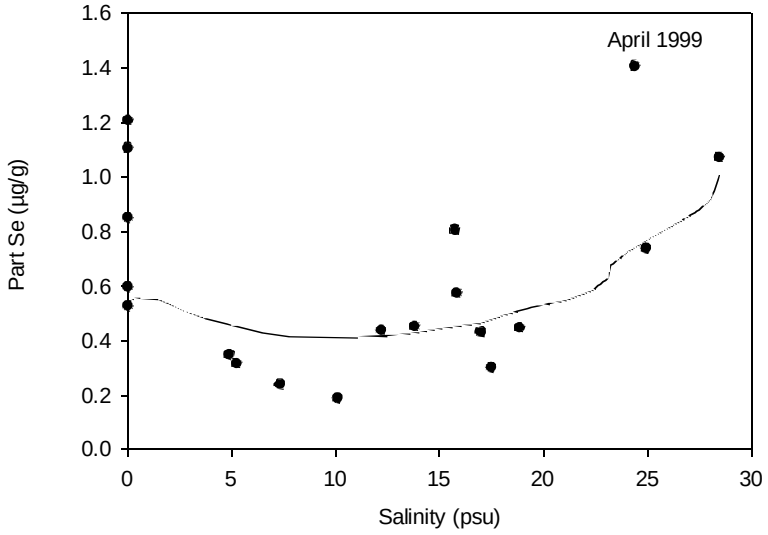

Figure 5-29
Model simulated particulate selenite and selenate, particulate elemental selenium, and particulate organic selenium compared to observed values compared to the April 1999 transect.

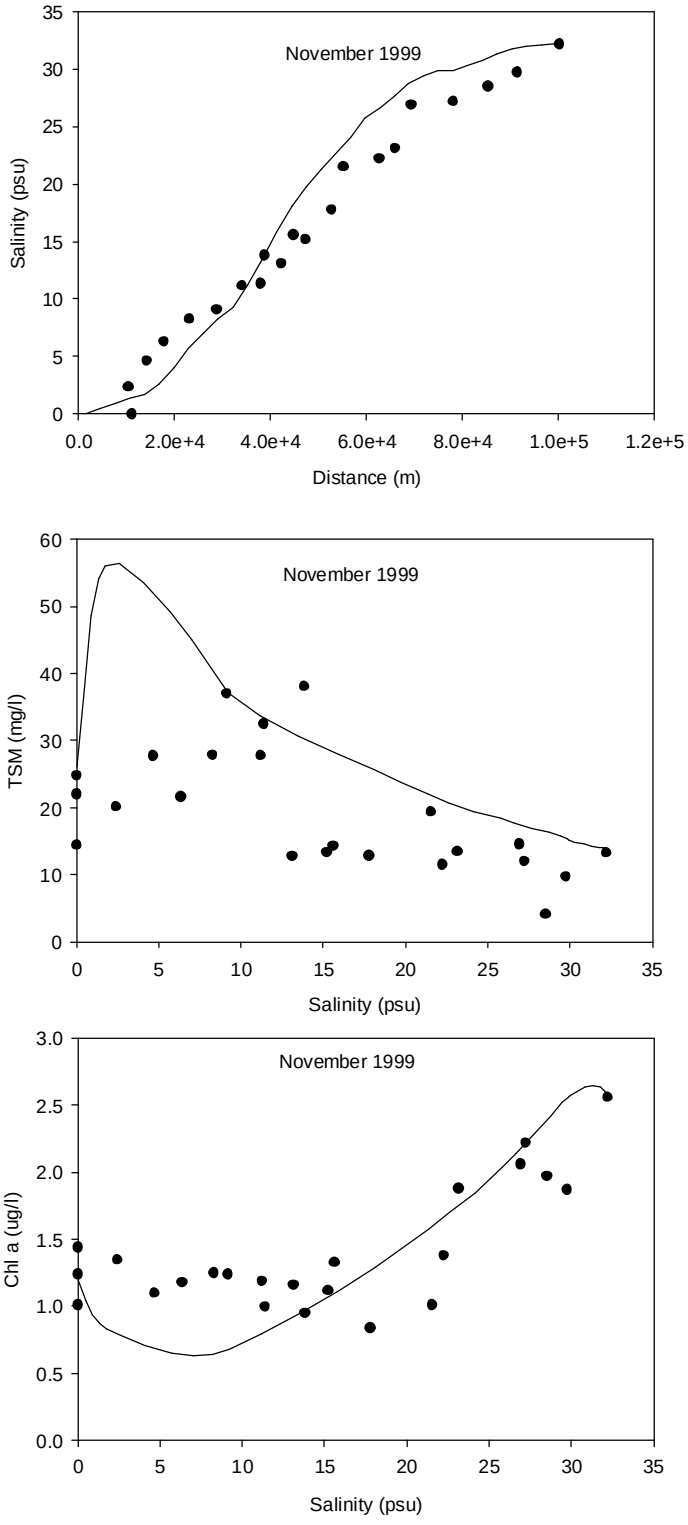

Figure 5-30
Model simulated salinity, TSM, and Chlorophyll a compared to observed values for the November 1999 transect.

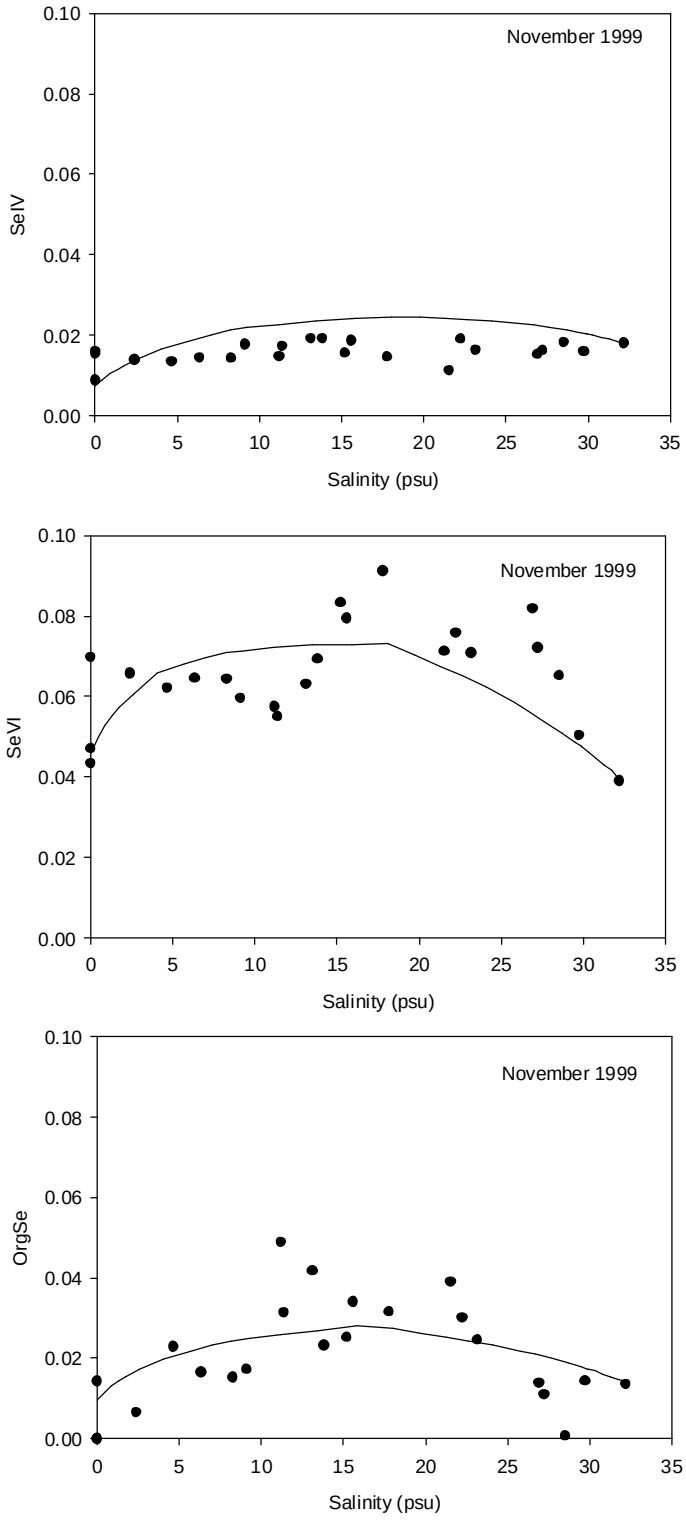

Figure 5-31
Model simulated selenite, selenate and organic selenide compared to observed values for the November 1999 transect.

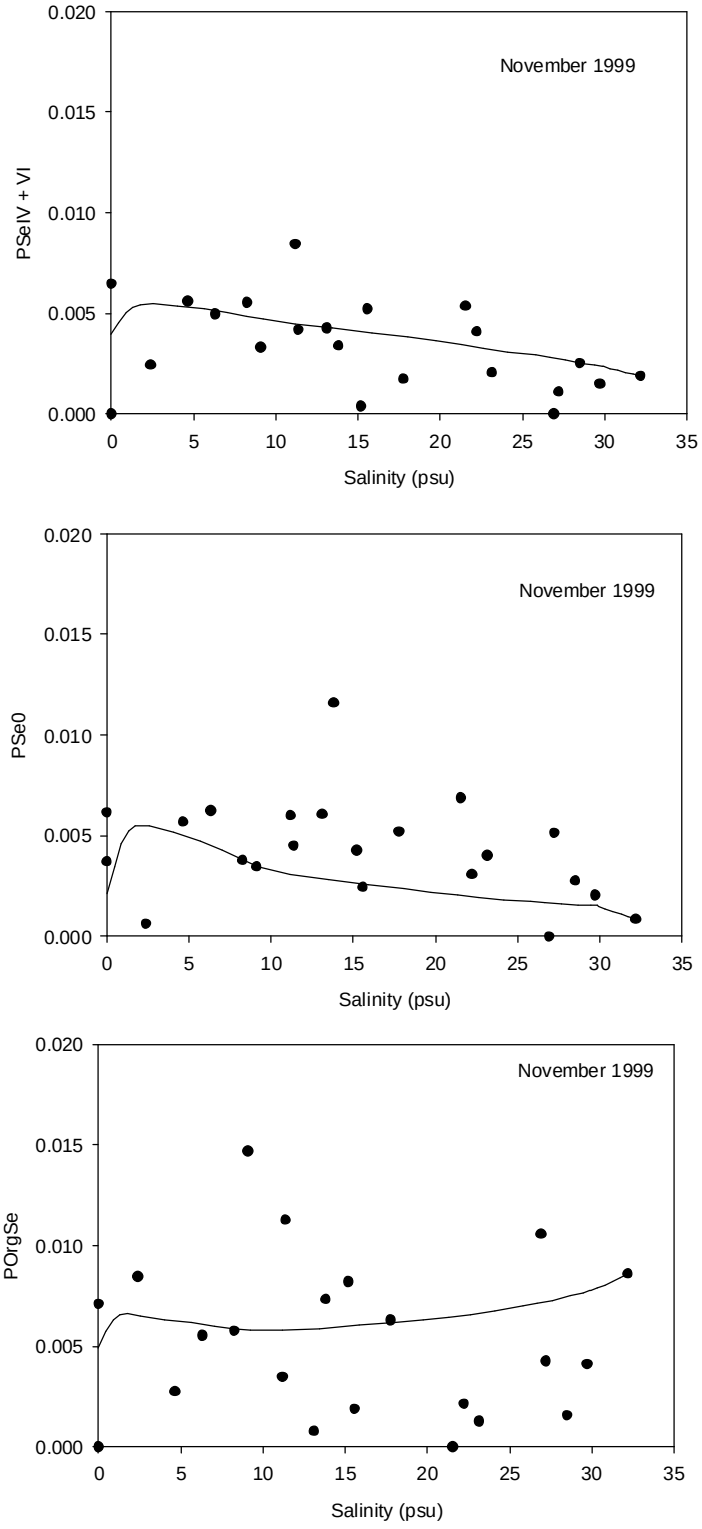

Figure 5-32
Model simulated particulate selenite and selenate, particulate elemental selenium, and particulate organic selenium compared to observed values compared to the November 1999 transect.

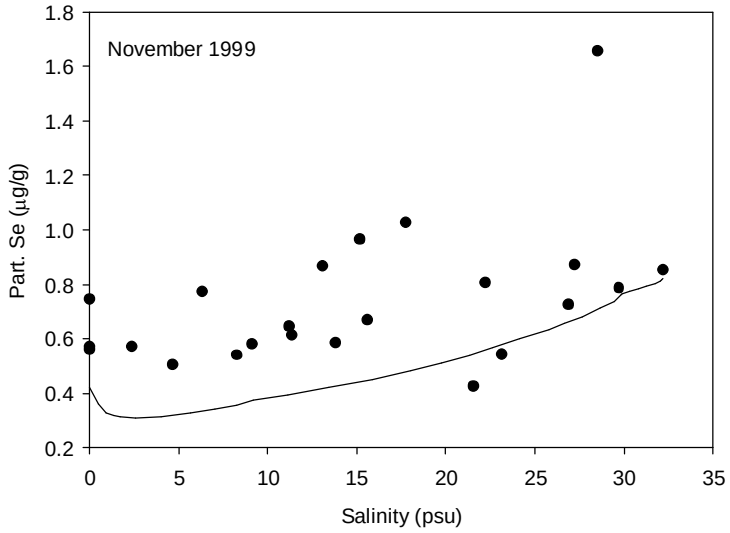

Figure 5-33
Model simulated particulate selenite and selenate, particulate elemental selenium, and particulate organic selenium compared to observed values compared to the November 1999 transect.

Table 5-5
Statistical Measures for Goodness of Fit for Simulations of April 1999 Transect

		Field salinity	Lab salinity	SeIV (ug/l)	SeVI (ug/l)	Total Dis. Se (ug/l)	Org Se (ug/l)	Chla (ug/l)	TSM (mg/l)	Total Part. Se (ug/l)	SeIV + VI (ug/l)	Se0 (ug/l)	Org Se (ug/l)	Part Se (ug/g)
MSE	optimal 0	14.94	281.87	0.0000	0.0005	0.0009	0.0009	3.53	269.73	1.3157E-04	4.2561E-06	8.5914E-06	0.0001	0.08
RMSE	optimal 0	3.866	16.789	0.003	0.022	0.029	0.031	1.880	16.424	0.011	0.002	0.003	0.008	0.290
PBIAS	optimal 0	16.288		-16.224	-7.170	-16.563	-27.605	36.718	17.255	59.829	24.974	67.126	57.445	8.600
GOF(%)		84.90		82.27	92.56	81.87	67.56	68.60	84.06	52.68	77.66	48.08	54.22	91.75
r		0.934		0.135	-0.128	0.320	0.020	-0.42	0.65	0.29	0.43	0.40	0.05	0.61

Table 5-6
Statistical Measures for Goodness of Fit for Simulations of November 1999 Transect

		Field Salinity	Lab Salinity	SeIV (ug/l)	SeVI (ug/l)	Total Dis. Se (ug/l)	Org Se (ug/l)	Chla (ug/l)	TSM (mg/l)	Total Part. Se (ug/l)	SeIV + VI (ug/l)	Se0 (ug/l)	Org Se (ug/l)	Part Se (ug/g)
MSE	optimal 0	6.16	6.16	0.00	0.00	0.00	0.00	0.22	87.78	0.00	0.00	0.00	0.00	0.06
RMSE	optimal 0	2.482	2.482	0.006	0.023	0.026	0.009	0.469	9.369	0.005	0.002	0.003	0.006	0.255
PBIAS	optimal 0	4.561	4.561	28.102	16.244	15.854	5.637	14.301	27.201	13.635	-1.010	-35.483	64.568	-8.488
GOF(%)		95.54	95.54	75.17	84.93	85.27	94.52	86.62	75.88	87.21	98.98	55.82	49.67	91.13
r		0.984	0.984	0.351	0.305	0.760	0.770	0.798	0.639	0.196	0.629	0.329	-0.195	0.472

Simulated Salinity, TSM and Chl a for the Period of 2010–2012

The model with updated salinity formulation and TSM calibration was validated against monthly cruise sampling data of physical parameters for the period of 2010–2012 (Figure 5-34 to Figure 5-42). The results suggest that the updated model is generally able to simulate salinity, TSM and chlorophyll a for a range of conditions during the period 2009–2012. For TSM, the model is able to capture the location and magnitude of the peaks in TSM, under a range of conditions, with a few exceptions under high flow (namely 03/2009, 01/2010, 02/2010, and 06/2010; Figure 5-37 to Figure 5-39). These exceptional cases may require further investigation. The simulation for chlorophyll a with one uniform formulation throughout is reasonable, as the model is able to simulate temporal variations in phytoplankton and most of all, spatial variations exhibited in different transects over time (Figure 5-40 to Figure 5-42). The quality of the fits associated with the ancillary parameters is shown in Table 5-7 through Table 5-9 and demonstrate the success of the model at capturing the ancillary parameter variability across a range of seasons and hydrologic conditions in 2009, 2010, and 2011.

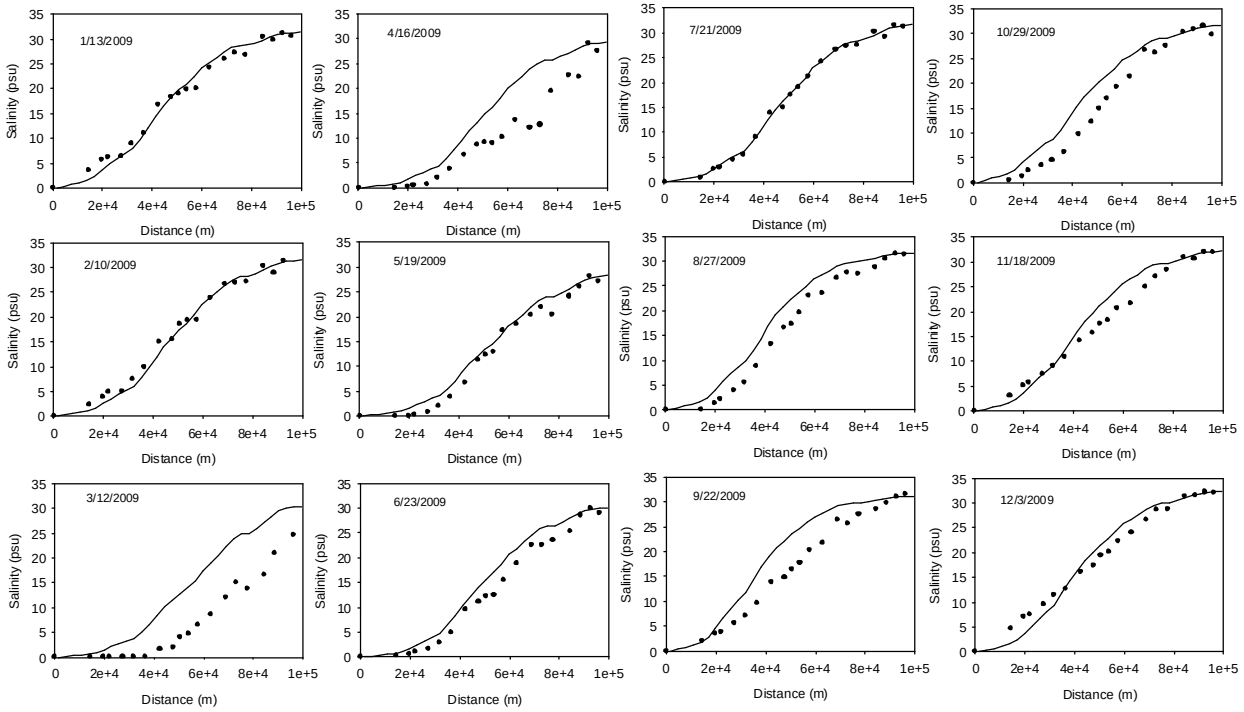

Figure 5-34
Model simulated salinity profiles compared to USGS monthly bay cruise sampling for 2009.

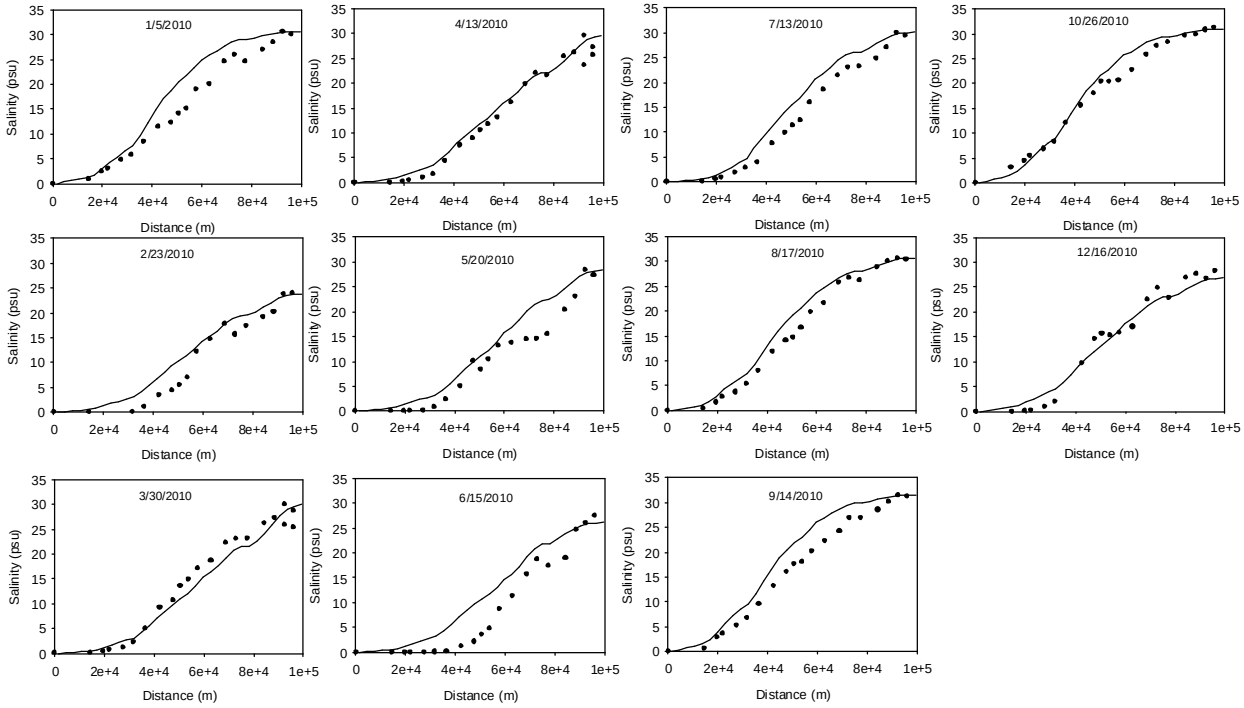

Figure 5-35
Model simulated salinity profiles compared to USGS monthly bay cruise sampling for 2010.

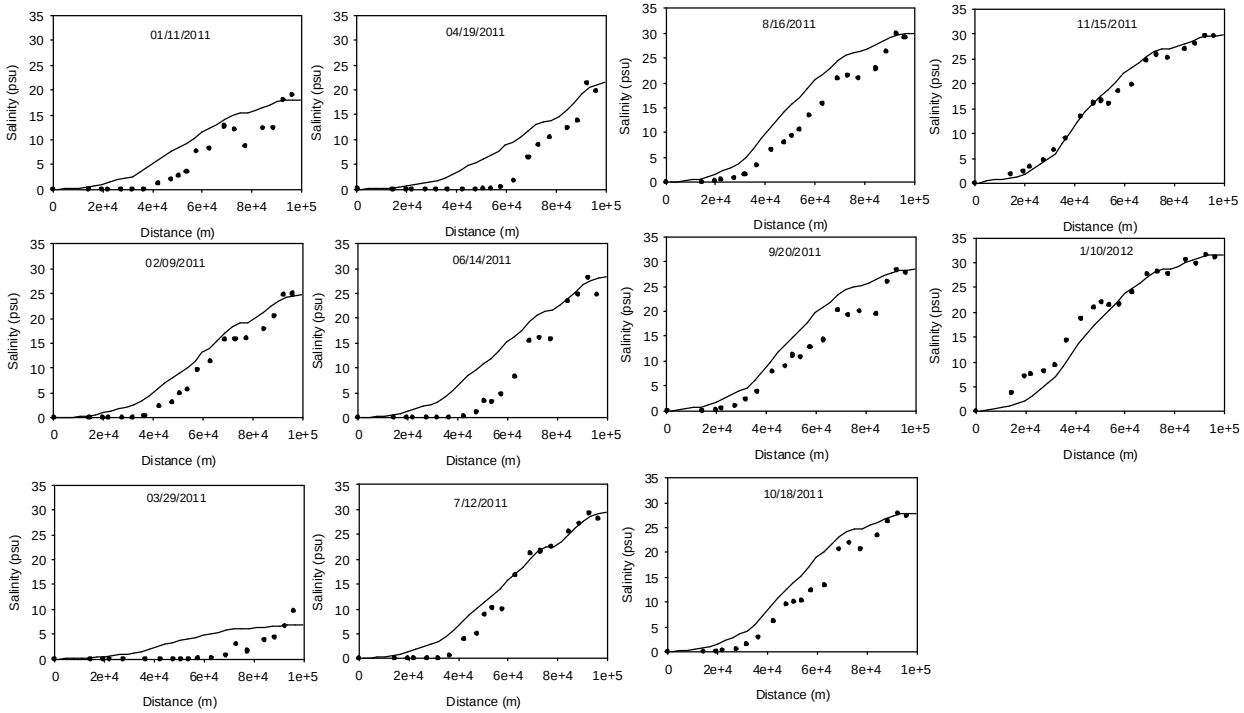

Figure 5-36
Model simulated salinity profiles compared to USGS monthly bay cruise sampling for 2011.

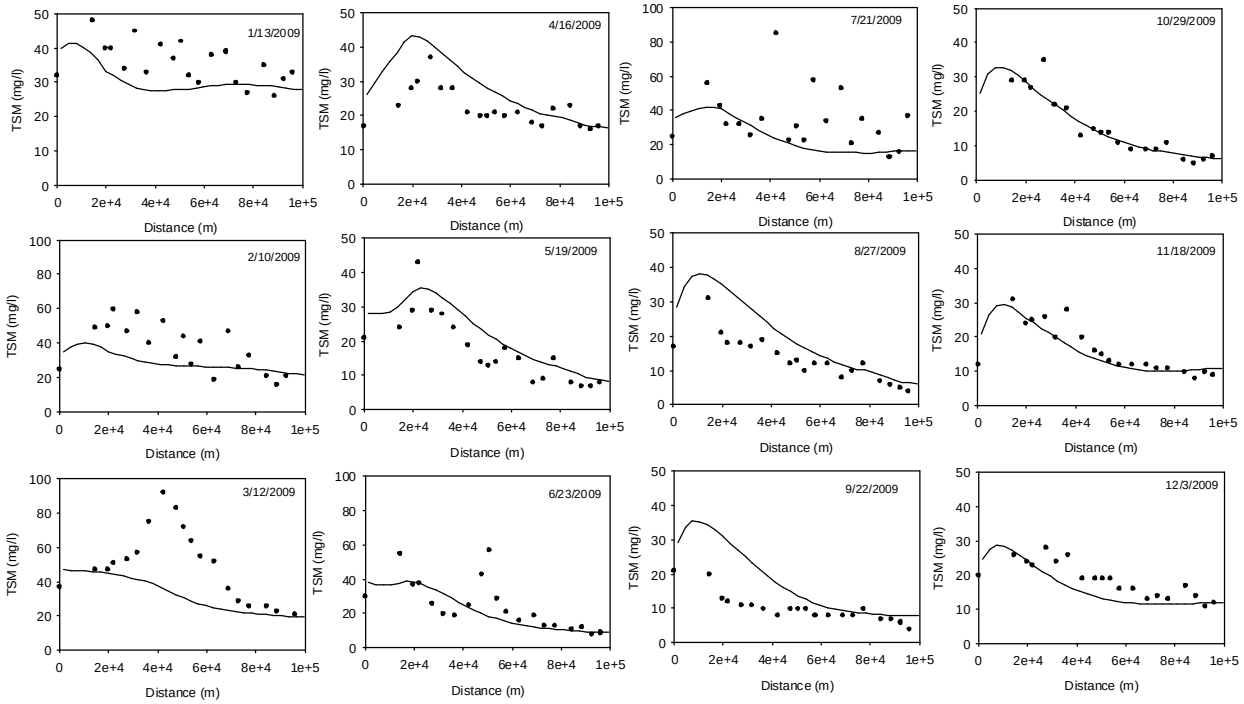

Figure 5-37
Model simulated TSM profiles compared to USGS monthly bay cruise sampling for 2009.

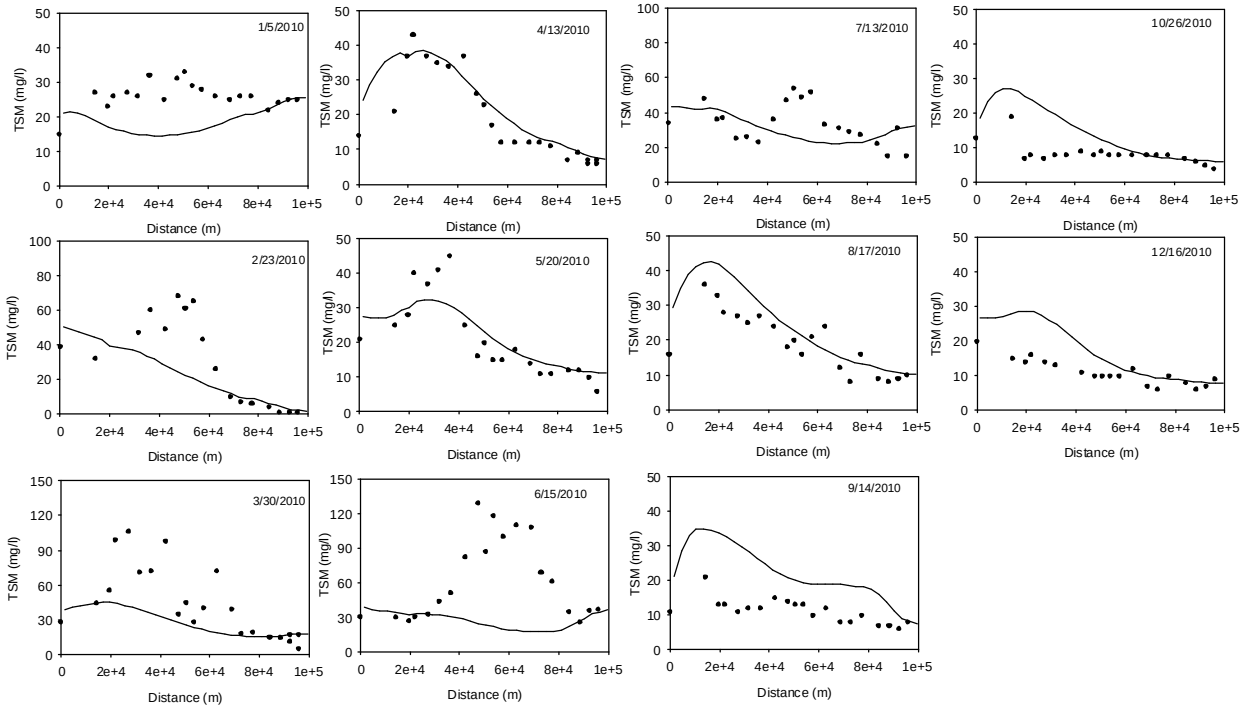

Figure 5-38
Model simulated TSM profiles compared to USGS monthly bay cruise sampling for 2010.

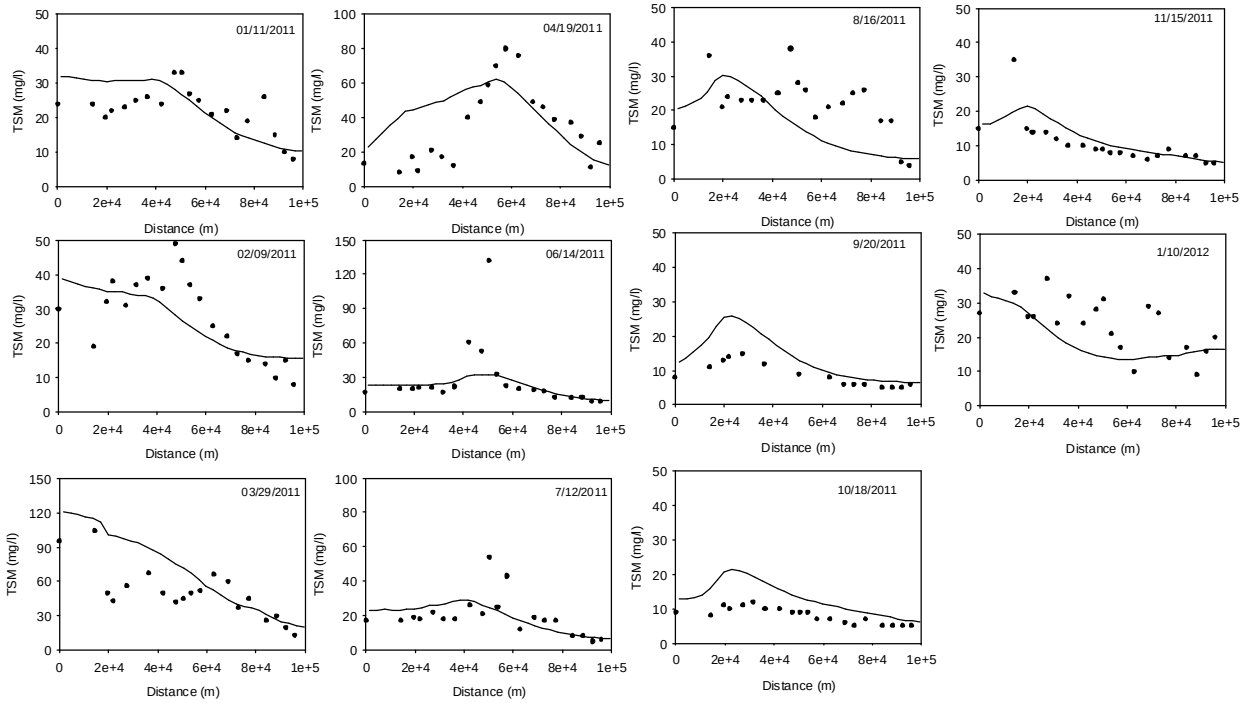

Figure 5-39
Model simulated TSM profiles compared to USGS monthly bay cruise sampling for 2011.

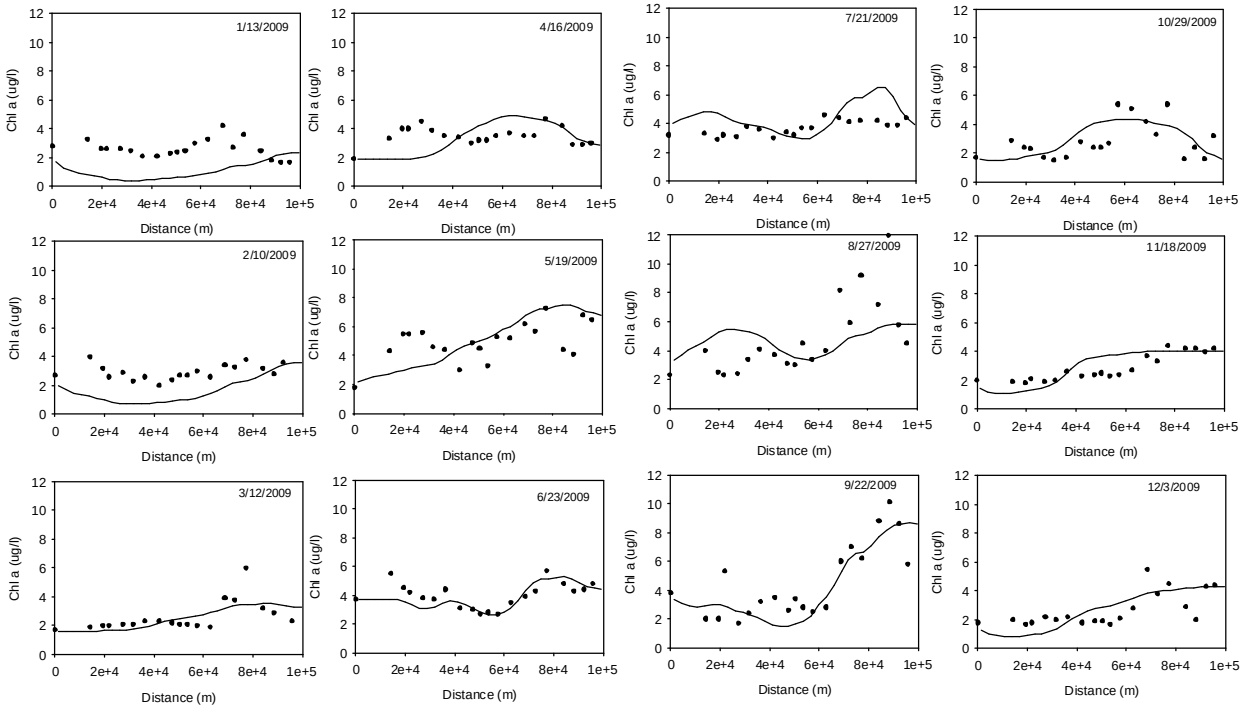

Figure 5-40
Model simulated chlorophyll a profiles compared to USGS monthly bay cruise sampling for 2009.

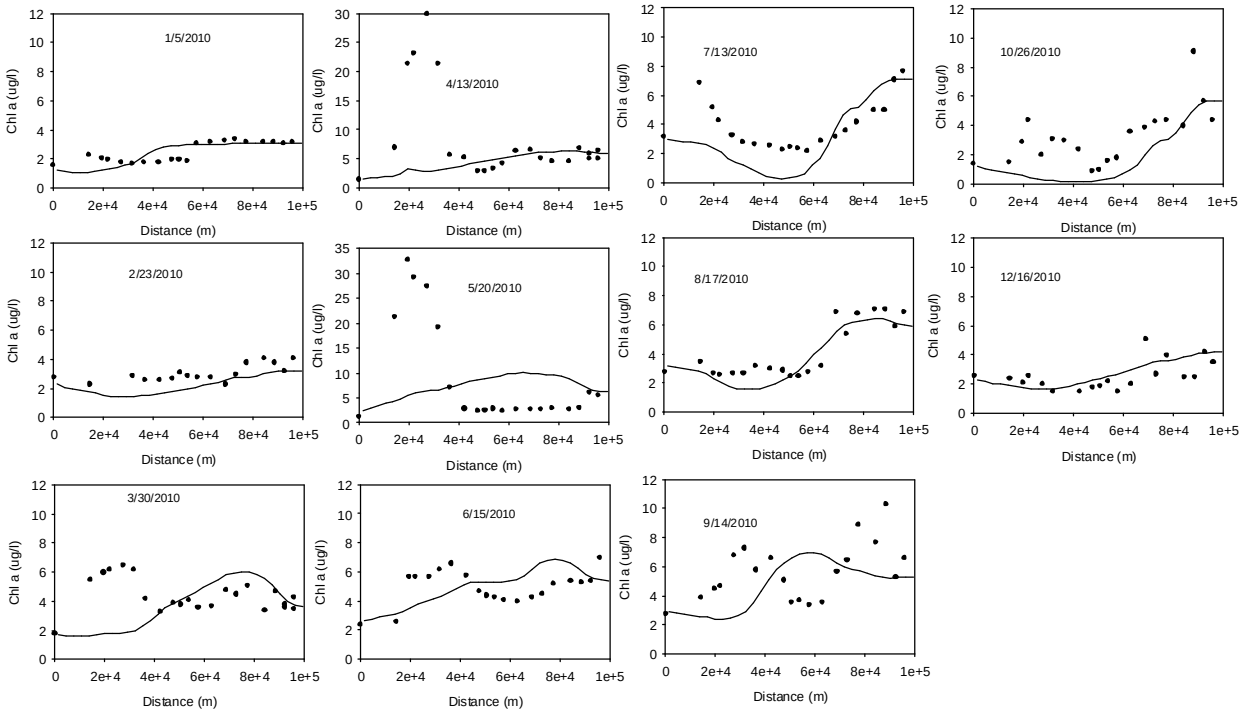

Figure 5-41
Model simulated chlorophyll a profiles compared to USGS monthly bay cruise sampling for 2010.

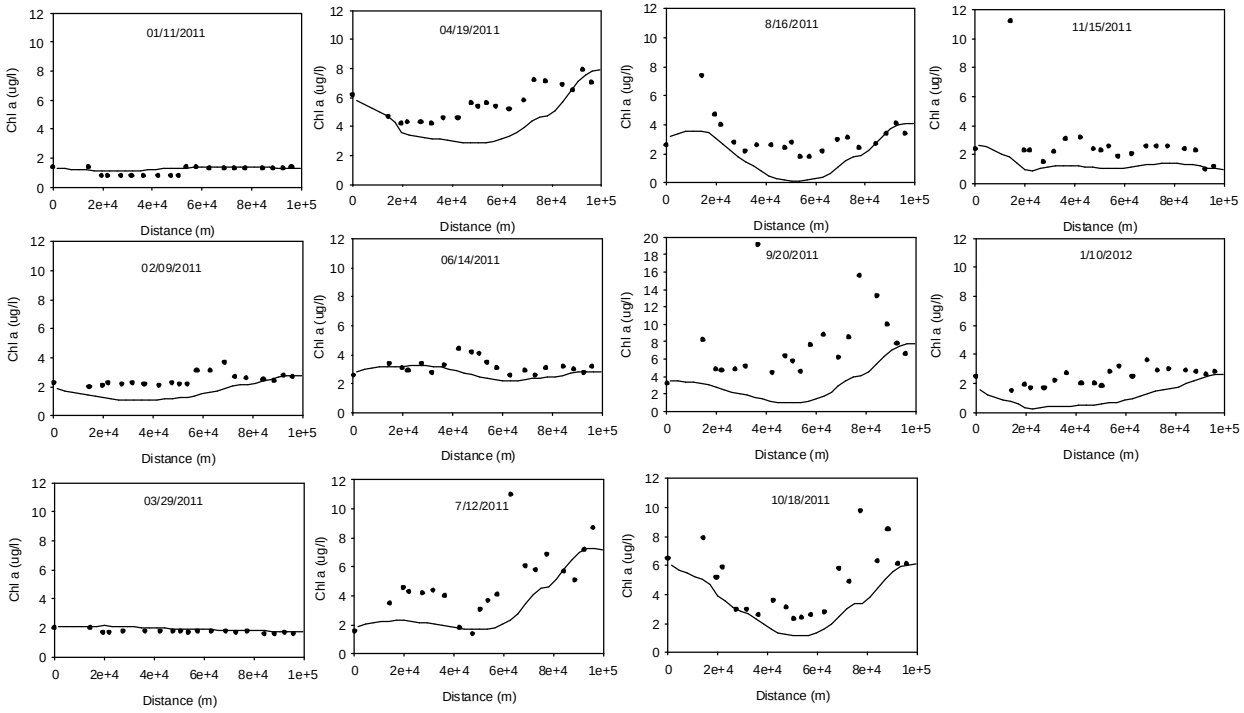

Figure 5-42
Model simulated chlorophyll a profiles compared to USGS monthly bay cruise sampling for 2011.

Table 5-7
Statistical Measures for Goodness of Fit for Simulations of Salinity for Period of 2009–2012

		1/13/2009	2/10/2009	3/12/2009	4/16/2009	5/19/2009	6/23/2009	7/21/2009	8/27/2009	9/22/2009	10/29/2009	11/18/2009	12/3/2009	1/5/2010	2/23/2010	3/30/2010	4/13/2010	5/20/2010
MSE	optimal 0	2.692	2.825	52.697	29.433	1.861	4.140	0.675	6.105	15.233	10.148	5.710	5.356	9.898	6.514	5.089	9.015	15.423
RMSE	optimal 0	1.641	1.681	7.259	5.425	1.364	2.035	0.821	2.471	3.903	3.186	2.389	2.314	3.146	2.552	2.256	3.002	3.927
PBIAS	optimal 0	-2.630	-5.710	87.309	43.328	6.555	10.829	-1.892	12.969	16.493	15.269	5.247	-2.034	13.740	15.070	-10.837	21.376	30.886
GOF(%)		97.334	94.070	36.165	67.868	93.650	89.713	98.090	87.831	84.719	85.802	95.714	89.232	87.116	86.021	88.523	80.634	73.003
r		0.994	0.994	0.958	0.944	0.995	0.992	0.998	0.994	0.968	0.984	0.982	0.987	0.980	0.979	0.990	0.975	0.966
		6/15/2010	**7/13/2010**	**8/17/2010**	**9/14/2010**	**10/26/2010**	**12/16/2010**	**1/11/2011**	**2/9/2011**	**3/29/2011**	**4/19/2011**	**6/14/2011**	**7/12/2011**	**8/16/2011**	**9/20/2011**	**10/18/2011**	**11/15/2011**	**1/10/2012**
MSE	optimal 0	5.134	3.272	7.406	2.726	3.493	128.215	12.520	6.382	8.611	16.070	24.299	5.366	14.365	12.186	8.429	2.063	10.084
RMSE	optimal 0	2.266	1.809	2.721	1.651	1.869	11.323	3.538	2.526	2.934	4.009	4.929	2.316	3.790	3.491	2.903	1.436	3.176
PBIAS	optimal 0	12.991	7.320	12.271	1.987	-4.409	-55.524	43.122	20.935	122.541	60.199	42.113	9.313	24.536	22.100	18.397	0.242	-10.748
GOF(%)		87.778	92.934	88.419	98.032	95.490	16.613	63.955	80.963	17.723	52.438	64.674	91.093	78.014	80.000	83.092	99.758	88.623
r		0.992	0.992	0.988	0.991	0.990	0.994	0.939	0.983	0.692	0.930	0.950	0.988	0.979	0.976	0.984	0.993	0.989

Table 5-8
Statistical Measures for Goodness of Fit for Simulations of TSM for Period of 2009–2012

		1/13/2009	2/10/2009	3/12/2009	4/16/2009	5/19/2009	6/23/2009	7/21/2009	8/27/2009	9/22/2009	10/29/2009	11/18/2009	12/3/2009	1/5/2010	2/23/2010	3/30/2010	4/13/2010	5/20/2010
MSE	optimal 0	42.155	112.813	468.869	133.829	79.395	162.261	442.400	146.709	191.255	35.503	26.808	31.605	65.539	297.663	771.409	43.550	2709.591
RMSE	optimal 0	6.493	10.621	21.653	11.568	8.910	12.738	21.033	12.112	13.829	5.958	5.178	5.622	8.096	17.253	27.774	6.599	52.054
PBIAS	optimal 0	-5.746	-14.049	-29.802	39.444	38.653	-6.158	-25.547	63.341	101.294	21.952	10.966	-0.099	-11.090	-24.248	-37.120	10.642	-56.191
GOF(%)		94.082	80.648	62.658	66.597	67.174	93.643	70.393	55.236	28.605	80.122	92.121	96.436	88.239	61.571	53.189	94.556	15.104
r		0.599	0.749	0.714	0.849	0.854	0.583	0.203	0.901	0.829	0.941	0.907	0.827	-0.350	0.836	0.792	0.844	-0.464
		6/15/2010	**7/13/2010**	**8/17/2010**	**9/14/2010**	**10/26/2010**	**12/16/2010**	**1/11/2011**	**2/9/2011**	**3/29/2011**	**4/19/2011**	**6/14/2011**	**7/12/2011**	**8/16/2011**	**9/20/2011**	**10/18/2011**	**11/15/2011**	**1/10/2012**
MSE	optimal 0	190.731	105.626	213.590	150.291	139.173	65.959	36.443	50.348	756.636	390.661	556.348	75.622	108.906	195.557	91.586	57.884	62.870
RMSE	optimal 0	13.811	10.277	14.615	12.259	11.797	8.122	6.037	7.096	27.507	19.765	23.587	8.696	10.436	13.984	9.570	7.608	7.929
PBIAS	optimal 0	-4.134	36.625	89.119	100.117	60.316	31.548	11.688	-0.344	33.962	23.007	-9.378	13.247	-13.508	170.717	102.913	42.187	-10.835
GOF(%)		95.778	68.666	35.196	29.227	52.363	76.831	88.941	99.656	67.849	79.256	90.149	87.552	85.476	-3.757	27.754	64.621	88.525
r		0.038	0.905	0.715	0.506	0.869	0.764	0.748	0.811	0.696	0.603	0.595	0.706	0.462	0.984	0.948	0.637	0.538

Table 5-9
Statistical Measures for Goodness of Fit for Simulations of Chlorophyll a for Period of 2009–2012

		1/13/2009	2/10/2009	3/12/2009	4/16/2009	5/19/2009	6/23/2009	7/21/2009	8/27/2009	9/22/2009	10/29/2009	11/18/2009	12/3/2009	1/5/2010	2/23/2010	3/30/2010	4/13/2010	5/20/2010
MSE	optimal 0	3.573	2.710	0.672	1.636	3.037	6.424	2.045	8.317	4.148	1.081	0.498	1.150	0.910	0.887	5.865	144.379	6.781
RMSE	optimal 0	1.890	1.646	0.820	1.279	1.743	2.535	1.430	2.884	2.037	1.040	0.706	1.072	0.954	0.942	2.422	12.016	2.604
PBIAS	optimal 0	-62.128	-47.838	-6.176	-11.523	-11.645	-58.628	-5.871	-45.359	-30.522	-8.645	-5.736	-3.875	-32.565	-25.957	-22.794	-30.597	-45.847
GOF(%)		-0.954	23.427	93.386	87.961	87.611	8.852	93.948	30.833	63.382	87.410	85.883	86.953	60.344	62.145	74.059	62.179	37.699
r		-0.258	0.535	0.619	-0.161	0.422	0.727	0.513	0.753	0.872	0.626	0.820	0.616	0.874	0.747	-0.556	-0.810	0.503
		6/15/2010	**7/13/2010**	**8/17/2010**	**9/14/2010**	**10/26/2010**	**12/16/2010**	**1/11/2011**	**2/9/2011**	**3/29/2011**	**4/19/2011**	**6/14/2011**	**7/12/2011**	**8/16/2011**	**9/20/2011**	**10/18/2011**	**11/15/2011**	**1/10/2012**
MSE	optimal 0	4.317	*1.211*	21.979	4.79	1.07	2.89	0.068	1.096	0.044	3.248	0.541	4.635	2.659	39.999	3.911	5.238	2.291
RMSE	optimal 0	2.078	1.100	4.688	2.188	1.034	1.700	0.260	1.047	0.210	1.802	0.736	2.153	1.631	6.324	1.978	2.289	1.514
PBIAS	optimal 0	-33.706	-17.350	-75.008	-51.468	-0.605	-49.426	14.928	-35.101	9.500	-25.967	-14.299	-20.204	-40.679	-61.045	-27.878	-48.987	-55.461
GOF(%)		58.602	80.916	-50.041	26.12	91.87	22.45	86.075	56.428	90.371	69.821	84.554	77.383	47.184	2.193	67.173	31.414	16.896
r		0.778	0.911	0.454	0.754	0.583	0.624	0.757	0.371	0.514	0.688	0.131	0.578	0.712	0.229	0.764	0.628	0.450

5.9 Summary

Given the dynamic nature of the various selenium species in the estuary, and with interactions between hydrology, suspended sediments, and phytoplankton that vary by season and year, this report focused on the use of a selenium geochemical model to help interpret the field data described in Section 4. This section presented an update of a model of selenium transport and transformation in NSFB reported earlier (Tetra Tech, 2010, Chen et al., 2012). This update benefited from the additional transect data collected during four sampling events from 2010-2012 as well as new data on inputs of selenium into the bay from the rivers, ocean, tributaries, and refineries, all characterized in the same manner as the transect samples. In addition to the data obtained through this sampling effort, the modeling also utilized the most recent supporting water quality data, on salinity, chlorophyll a, and total suspended material, reported monthly by the USGS over the entire period of the study. These supporting water quality data helped to evaluate the performance of related components of the model under a much broader range of conditions than would be possible using the transect points alone.

The model was used with essentially the same set of transformation rates that had been applied in earlier work, with two exceptions: there was a change to the salinity calculation methodology and a modification of the rate constant for phytoplankton selenium uptake. The performance of the model, as represented by its ability to fit multiple water quality metrics simultaneously, was characterized by a suite of statistical estimates that can be used to identify the metrics or periods where the model performs best, and where there are processes that are not fully captured by the model.

Important findings from the modeling update are as follows:

- With the addition of measurements of selenium concentrations and selenium speciation data for refineries and tributaries over 2010-2012, the model has a more credible basis for representing these inputs. In previous work, these inputs were estimated from a variety of sources that were either dated or did not use the same analytical methods that were applied in the estuary samples.
- A modification was made to the methodology for estimating salinity in the bay under different flow conditions. The updated model is able to simulate salinity well, under a range of conditions from 2009–2011, describing the basic seawater-freshwater mixing in the estuary that also controls dissolved selenium transport. Table 5-7 presents a summary of the salinity fits over this period, and this quantity is the best described of the ancillary parameters (with goodness of fit, between observed and modeled values often exceeding 80%). This is not surprising because salinity is controlled by large scale forces such as net outflow from the bay that are well represented in the model.
- The total suspended material (TSM) values from 2009-2012 (transect values as well as monthly USGS values) are not captured as well as the salinity data because these are affected by more local drivers than salinity, such as tidal and wind-driven resuspension that are not fully captured in the one-dimensional model used. The location and magnitude of TSM peaks are represented moderately well by the model. However there are occasions where the estuarine turbidity maximum (ETM), representing a balance between tidal resuspension and settling of riverine particulates in saline waters, is under-predicted for some periods. The value of the goodness of fit, between observed and modeled values, is lower than for salinity and in the 60-90% range for most dates, Table 5-8.
- In a manner similar to that for TSM, chlorophyll a values are described moderately well (with goodness of fit between observed and modeled values, between 60-90% for most

dates, Table 5-9). As with TSM, and unlike salinity, chlorophyll a values are likely to be influenced by local effects in space and time such as phytoplankton blooms or differing grazing rates that are not used in the one-dimensional model applied here.

- Despite the limitations of the ancillary parameter modeling, it is important to emphasize that a reasonable representation of these parameters, as applicable to a broader understanding of selenium behavior, was achieved through this process.
- Based on data and fits across six transect periods from 1999-2012 (Tables 5-1 through 5-6), of the dissolved selenium species, total selenium is best represented by the model, followed by selenate and selenite. Organic selenide is less well represented, in part because it is a more noisy quantity in the analytical determination (it is estimated by difference of total selenium and selenate+selenite).
- In general, over the 1999-2012 period of the study, particulate species are fit less well than dissolved species (Tables 5-1 through 5-6) with poorer fits for individual species than for total particulate selenium. This is related to the complexity of the underlying processes, due to the independent influences of TSM and chlorophyll a on particulate selenium, as well as the variability in the reported data that was discussed in Section 4. Thus, particulate selenium species often display considerable variation between adjacent stations sampled on the same day, a pattern not seen with the dissolved species.
- The focus of the current effort was an improved representation of selenium speciation in the bay under varying conditions over the study period. Although the model formulation and parameters used to describe the 2010-2012 conditions were largely unchanged from those developed based on the 1999 data, this points to the robustness of the original calibration and its ability to reasonably represent the driving processes controlling selenium speciation in the estuary. The data and analysis in the present report provide support for this use of this model in future steps of the selenium TMDL, where there is a need to link loads to biological endpoints of concern. This report, however, does not address two issues that may be considered in future phases of the analysis: estimation of tissue concentrations in the study period and calculation of concentrations under changing loads. No public data are available on tissue concentrations post February 2010, to allow model evaluation as done for water column concentrations. Tissue concentrations prior to 2010 have been described previously in Chen et al. (2012).

While these new analyses make a significant contribution to the understanding of the sources and behavior of selenium in North San Francisco Bay, several opportunities exist for improving the knowledge base through the collection of new data as part of routine monitoring programs and focused studies.

- The initial modeling results conducted as part of the TMDL effort (Tetra Tech, 2010) identified the importance of particulate selenium concentrations at the boundary locations (Freeport and Vernalis) on the use of the ECoS model predictions of particulate concentrations in the estuary and the levels of expected bioaccumulation. Prior to the sampling conducted in 2010 – 2012 as part of the Se Characterization Study, there were only 3 measurements reported in the literature at Vernalis, and none at Freeport. In the 2010 – 2012 wet- and dry-weather sampling events 10 additional measurements were made at these locations combined. Together these historical and recent data justify the initial model parameterization and support the use of the modeling framework for the TMDL. Given the demonstrated importance of riverine sources of particulate selenium concentrations, more frequent sampling at the boundaries should be considered to monitoring long-term trends and seasonal variability.

- The magnitude of the source and the chemical transformations of Se from the Sacramento and San Joaquin Rivers to the Delta and within the Delta are not well understood. Data collected within the Delta (Rio Vista and Jersey Point in this study) reflect mixing within the Delta and influence from the Bay, and therefore do not reflect changes from the sources to the Delta (e.g., from Vernalis to Jersey Point or from Freeport to Rio Vista). A Delta removal constant was assumed for each dissolved species, similar to the approach in Meseck (2002) and in the previous model. However, this is an important and consequential assumption of the model. Given the importance of the riverine sources of selenium on bioaccumulation and the potential changes in the riverine inputs associated with Delta conveyance proposals, better characterization of the magnitude of the Se sources and transformations within the Delta are warranted.
- As noted above, the local variation of particulates in the bay (caused by sediment resuspension or phytoplankton blooms) are not fully represented by the model. As an example, one of the sampling events showed higher particulate concentrations than all other events (September 2010). This affects selenium particulate concentrations in the water column, although the effect may be occasional and not continuous. A better understanding of the role of the estuarine particulate variation, possibly derived from related bay-wide studies on phytoplankton and suspended sediments, may allow improved characterization of particulate selenium. In the near term, however, the use of selenium concentrations normalized to TSM (in µg/g) may be used to address uptake by filter feeders.

6 Discussion and Conclusions

Prior to the inception of this work, studies in support of the selenium TMDL development in North San Francisco Bay noted that there were no speciation data on selenium for nearly a decade (from 1999 to 2010), despite changes in point and non-point loads over this time (Tetra Tech, 2008). There were also no data on speciation of selenium in the riverine and ocean boundaries of the estuary, particularly data on particulate selenium, which was identified as a component that was important in controlling its uptake into filter feeders and into benthic predator species. These data gaps have been substantially filled through the data collection and analysis presented in this report. The data provide information on loads and in-estuary concentrations under current conditions, and represent characteristic seasonal patterns of the region, with two sampling events each in the wet and dry seasons over 2010 through 2012.

An additional objective of this work was to update the modeling of selenium previously performed for the bay (Tetra Tech, 2010; Chen et al, 2012). A major effort of the original modeling was to estimate selenium transformation and uptake rates to describe the concentrations observed in the bay, focusing on data from 1999, but also considering a broader dataset from 1987, as well as unspeciated selenium data to 2005. This parameter estimation or calibration process is strongly dependent on the data used, and the new data provides an important test and an opportunity to refine the model. Model load inputs were updated using new point source and riverine boundary data. With the inclusion of two changes, one for the computation approach for the salinity concentrations in the bay, and a second for the phytoplankton uptake rates of selenium, the model was able to describe key features of the data in the bay over the four sampling events. This new work provides additional support for the use of the model in informing management actions related to selenium in the San Francisco Bay region.

Specific elements of the study and the relationship to permit requirements discussed in the Introduction are discussed in greater detail below.

6.1 Transect Sampling

Given the similarity between prior sampling in 1999 and the 2010–2012 sampling, the data obtained in this work were compared directly with the prior data, and allow examination of changes over the preceding decade. For this report, both the dry weather and wet weather sampling results were included, and different results were found for dry weather and wet weather sampling, as also for the two years of sampling. It was noted that the 1999 and 2011 dry weather sampling events showed similar results, with the 2010 dry weather event being distinctly different.

Particulate selenium concentrations are important as selenium in this phase can be taken up directly by clams for bioaccumulation across the food chain. For the dry weather, the data indicate that particulate Se concentrations in the North San Francisco Bay are lower by a factor of two in the September 2010 sampling event compared to November 1999 and October 2011 across most of the bay, especially for salinities above 10 g/l. The particulate environment in the water column in September 2010 is quite different from that in November 1999/October 2011, with higher TSM concentrations and a lower proportion of planktonic material in the mix, as

represented by the lower chlorophyll a/TSM ratio. TSM data are collected on a regular frequency by the USGS, and these show considerable variation over weeks even during the dry season, possibly driven by local events including winds. This implies that dry season particulate selenium concentration can vary over short time frames that are not easily captured in once-a-season transect sampling events.

Kd values, representing the ratio of particulate to dissolved selenium concentrations, are lower in September 2010 than in November 1999/October 2011 by a factor of 2 to 3. This demonstrates the complexity of selenium partitioning and its relationship to variability in TSM. These calculations show that any given snapshot of selenium distribution in different environmental media should be treated with caution, and that the ratio of particulate to dissolved cannot be assumed to remain fixed over changing conditions, which may include, among other things, changing sources, phytoplankton abundance and species, dissolved and particulate selenium speciation, and also seasonal and long term hydrological changes.

For the wet weather sampling, the transect sampling suggested relatively unchanged dissolved selenium concentrations by species during high flow periods of March 2011, April 2012, and April 1999. The most significant change is the decrease in dissolved organic selenide in March 2011 compared to the other two events.

6.2 Riverine Boundary Conditions

For both dry weather and wet weather sampling events, the San Joaquin River boundary value of particulate Se in µg/g is about twice that of Sacramento River at Freeport. The San Joaquin River is widely understood to represent more contaminated conditions for selenium, and the Sacramento River is thought to represent background conditions. Given this consideration, the range of particulate concentrations is fairly narrow, and because the flow in the Sacramento River is much higher, the role of the Sacramento River in influencing the level of particulate selenium in the system is significant. As shown for the dry weather sampling, particulate selenium in µg/g from the San Joaquin River boundary is higher than all samples collected in the estuary. This suggests that during low flow conditions high particulate selenium from the San Joaquin River may be a large contributor to the estuary. Compared to the riverine boundary condition used in previous work (Tetra Tech, 2010), particulate concentrations in µg/l at Rio Vista and at Freeport are similar, although concentrations in µg/g are slightly lower at Rio Vista than at Freeport.

6.3 Coastal Boundary Conditions

Because inflows from the ocean are an important contributor to in-estuary conditions, it was important to characterize the selenium speciation in the coastal zone. Such data have not been reported along the Pacific coast. Samples collected from the coastal zone as part of this study form an important contribution to the overall understanding of selenium in the San Francisco Bay region. The data show total dissolved selenium concentrations at levels similar to the Sacramento River boundary with selenate being the dominant component, followed by selenite and very low levels of organic selenide. Particulate selenium concentrations in the coastal zone, expressed as µg/g, on the other hand, were fairly high, and in one instance, higher than all estuary concentrations. These data are consistent with estuary data in the dry season that show an increase of particulate concentrations toward the seaward end of the estuary (in two of three sampling events).

6.4 Receiving Water

Sampling near the refinery outfalls was challenging because of the need to locate the samples within a few meters of the diffusers. The results showed elevated concentrations for dissolved selenium compared to receiving water in the vicinity of these stations, for both dry weather and wet weather events. However, this was not the case for particulate selenium concentrations, which were in line with the estuary concentrations.

Dissolved selenium concentrations in the receiving waters near refinery outfalls are elevated relative to concentrations sampled in the estuarine transect for selenite, selenate and total selenium.

6.5 Refinery Effluent

Refinery effluent selenium is mostly in dissolved form, with a small fraction of particulate selenium. Dissolved selenium concentrations in the effluents are generally in the form of selenate. Particulate selenium concentrations in the refinery effluents are dominated by particulate elemental selenium.

6.6 Modeling Results

The modeling presented in this work focused on mid-estuary data on the different selenium species. The modeling approach used is one-dimensional, where the estuary is represented as a series of 33, 3-km wide cells from Rio Vista in the Sacramento River/Delta to the Golden Gate. The modeling approach is suited for larger scale processes, and small scale features of the data, such as the concentrations near the refinery discharge cannot be represented through this model.

As a general summary, the model was able to represent the observations of both dissolved and particulate selenium across six different events spanning a decade (4 current, and two from 1999) and different loading and hydrologic conditions. This was done using updated model inputs, but largely unmodified selenium transformation rates. The sole change in uptake rates related to the phytoplankton uptake of selenium. However, due to simplifications in the model, local variations in particulate selenium are not always captured. These may be caused by local variations in phytoplankton growth and resuspension of sediments that are not represented in the model.

6.7 Relationship to Permit Requirements

The six elements identified the permit are addressed as described below:

a) Sampling results, data interpretation, and conclusions, such as receiving water and mixing zone characterization, seasonal variability, etc. This information is presented in the report chapters and the supporting appendices.

b) Effluent characterization. The monthly effluent samples and the receiving-water samples provide information on the dissolved and particulate speciation of the discharged selenium from refineries.

c) Determination if there is reasonable potential for selenium in the discharge to violate the Basin Plan's narrative bioaccumulation objective through the use of pertinent models. Data on receiving water concentrations, obtained in proximity to the discharge locations are described and compared with concentrations observed at mid-estuary locations. The modeling described in this work is performed on an estuary-wide scale, but the receiving water data may be utilized for near field modeling.

d) Comparison of near-field selenium water column concentrations to applicable numeric objectives. The current water column objective of 5 µg/l is not exceeded in the near field concentrations sampled over four periods. The water column objective is currently under review.

e) Demonstration of spatial and temporal extent to which the objectives and other relevant guidelines, are being exceeded. Total selenium data are presented over the transect across different seasons for direct evaluation against specific numeric objectives. All concentrations in the Bay are below the 5 µg/l water quality criterion.

f) Determination whether selenium levels impact foodweb and wildlife and/or contribute to bioaccumulation. The ECoS model application as previously developed and calibrated (Tetra Tech, 2010) was evaluated for the new conditions, utilizing the most current information on inflows and selenium loads from point and non-point sources. The modeling was updated to compute through 2012, among other elements, the particulate selenium concentrations, the pathway through which selenium uptake in benthic feeding organisms occurs. This updated modeling with the new data is a more robust tool for evaluating the bioaccumulation in the bay, and the linkage between sources and biota concentrations. Previously published work described selenium bioaccumulation in clams, fish, and birds (Chen et al., 2012); however no new data on these compartments have since been reported to assess conditions in 2011 and 2012.

6.8 Next steps

The integration of modeling and the most recent data is a major addition to the knowledge base for developing a robust selenium TMDL for San Francisco Bay. In this work the updated model has been compared to the most recent water column data, but no post-2010 data on tissue concentrations (in clams, fish, or birds) were publicly available. An important addition will be the comparison of model estimates with data for tissue concentrations in the bay.

Although some refinement in the modeling can be envisioned as outlined in Section 5, the present state of the model is suitable for use in developing scenarios for the TMDL, including evaluation of changing loads and their effect on endpoints of interest such as water column concentrations and tissue concentrations. Future work by the Regional Board may consider the implications of multiple scenarios on endpoints of regulatory interest.

Continued data collection in the estuary in the future through the Regional Monitoring Program, will also be beneficial. Such sampling may focus on a subset of in-estuary stations, but representing the riverine and oceanic boundaries. The boundary values are emphasized because despite the new data presented here, these measurements have only been obtained for a small number of points and represent a limited range of conditions.

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