Total Maximum Daily Load
Selenium in North San Francisco Bay

Preliminary Project Report

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San Francisco Bay Region
January 2011

For details of technical analysis, data interpretations and model development in support of the TMDL see Technical Memoranda prepared by Tetra Tech Inc.:

Technical Memorandum 2:	North San Francisco Bay Selenium Data Summary and Source Analysis. July 2008.
Technical Memorandum 3:	North San Francisco Bay Selenium Toxicological Assessment. April 2008.
Technical Memorandum 4:	Conceptual Model of Selenium in North San Francisco Bay. August 2008.
Technical Memorandum 5:	Recommendations for Numerical Model Development. August 2008.
Technical Memorandum 6:	Application of ECoS3 Model for Simulation of Selenium Fate and Transport in North San Francisco Bay. February 2010.

These Reports are available on San Francisco Bay Water Board website:
http://www.waterboards.ca.gov/sanfranciscobay/water_issues/programs/TMDLs/seleniumtmdl.shtml

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1 INTRODUCTION

This Preliminary Project Report summarizes the data and supporting information acquired over the past three years, and provides interpretation of technical analyses conducted to support development of a Total Maximum Daily Load (TMDL) to address and reduce selenium impairment in the North San Francisco Bay (North Bay).

The report presents a scientific basis for the proposed numeric target for the TMDL, protective of human health, wildlife and aquatic life, and contains the results of impairment assessments, sources and loadings analysis, and linkage analysis. A modeling framework for simulation of selenium transformations and biological uptake processes in the North Bay comprising a numerical estuary model and a bioaccumulation DYMBAM model is also discussed. In the following sections the available data and information on the key processes and conditions leading to the impairment are presented together with the information gaps and uncertainties identified while conducting the technical analyses.

Additional data collection and interpretation of information that will likely become available over the next two years are recommended before the final decision could be made about how to proceed with this TMDL.

2 PROBLEM STATEMENT

San Francisco Bay is listed under section 303(d) of the Clean Water Act as impaired for selenium because bioaccumulation of this element has led to recurring health advisories for local hunters against consumption of diving ducks. Moreover, elevated selenium concentrations found in biota often exceed levels that can cause potential reproductive impacts in white sturgeon and are often higher than levels considered safe for fish and other wildlife species in the estuary.

The problem has been somewhat exacerbated by the introduction of the Asian clam (*Corbula amurensis*) into the Bay in 1986. This non-native clam is a prodigious filter-feeder, and by consuming large quantities of selenium-laden particles this exotic species provides a pathway for biotransformation of a considerable mass of selenium into the benthic food web and thus to diving ducks and large fishes such as sturgeon. The estimated whole body selenium concentrations found in sturgeon often exceed the proposed draft United States Environmental Protection Agency (USEPA) limit of 7.91 µg/g (USEPA 2004) and are above the level of concern (4-12 µg/g) indicated by the US Fish and Wildlife Service recommended ecological risk guidelines (Presser *et al.* 2004). Increased levels of selenium in the Bay-Delta have been recognized as a possible contributing factor to the observed decline of some key species, e.g. white sturgeon, Sacramento splittail, starry flounder and surf scoter.

Sources and pathways leading to the possible impairment in northern and southern segments of the Bay differ significantly and therefore a separate approach to addressing the problem is warranted. The widespread selenium food web enrichment is most pronounced in northern segments of the Bay extending from the Delta to the Central Bay, while Lower and South Bay segments indicate only a localized enrichment. The northern segments of the Bay are dominated by the freshwater inflows from Sacramento and San Joaquin Rivers that contribute substantial amounts of selenium enriched sediment and irrigation runoff from Central Valley. The Lower and South Bay segments receive much lower freshwater inflows and the observed selenium levels appear to be dominated by groundwater discharges and dewatering operations.

Thus, this TMDL is being developed for the North San Francisco Bay segments (North Bay) only, which for the purpose of this project include a portion Sacrament/San Joaquin Delta, Suisun Bay, Carquinez Strait, San Pablo Bay and Central Bay (Figure 1). It aims at identifying sources and prioritizing management practices that could lessen possible detrimental effects of selenium on wildlife and, subsequently, will lead to reducing selenium concentrations in fish tissue to the levels that are, to best of our knowledge, safe and protective of beneficial uses. When completed the TMDL will include the fish tissue-based numeric target and associated total daily maximum loads, allocations, and implementation actions.

2.1 Basis for 303(d) Impairment Listing

In 1987, the California Department of Health Services issued a human health advisory against consumption of two species of ducks (Greater scaups and Surf scoters) from the Bay-Delta area due to elevated concentrations of selenium in tissue of the waterfowl. This advisory reflected the impairment of San Francisco Bay beneficial uses and provided a means for placing the Bay on the 303(d) list of impaired water bodies. The health advisory was based on the initial results reported by the Selenium Verification Study that begun in 1985 (SWRCB 1991).

The purpose of the Verification Study was to provide a comprehensive assessment of selenium and trace elements in a wide array of aquatic and terrestrial organisms from previously identified areas of concern. The selenium contamination was measured in 26 locations throughout the state including the areas in the San Francisco Bay and the Delta. The results of the study showed very high concentrations of selenium in scoters (more than 30 µg/g wet weight in liver) as well as elevated levels of selenium in muscle tissue of white sturgeon (average of 4.1 µg/g wet weight). The levels of selenium in scoters were three times higher than those determined by the US Fish and Wildlife Services (USFWS) to cause selenium toxicosis and reproductive impairment.

Figure 1: Segments of San Francisco Bay

The study also found high concentrations of selenium in clams and other animals that are a source of food for these migratory waterfowl and certain larger fishes. On average selenium concentrations in the muscle of white sturgeon, which feeds primarily on benthic organisms were five times higher than, for example, in striped bass, which are primarily piscivorous. The study concluded that food habits played a role in selenium accumulation, and that the species with elevated levels of selenium in their tissue were either bottom-dwellers or species with diets comprising of benthic organisms.

As a result of the elevated selenium levels in wildlife and the issuance of the health consumption advisory, the 1998 303(d) list identified San Francisco Bay as impaired by selenium. The current 303(d) list (2010) continued the listing of most segments of the Bay (see Table 1). Despite the fact that the Bay was listed as impaired prior to adoption of the Water Quality Control Policy for developing California's Clean Water Act Section 303(d) List (2004) the listings are consistent with the current policy. The listing factors, among others, include a health advisory against the consumption of edible resident organisms and bioaccumulation of pollutants in aquatic life tissue.

Table 1: The San Francisco Bay segments listed as impaired by selenium

San Francisco Bay segment or Water Body		2010 303(d) List	Indicator of Impairment
North Bay	Sacramento-San Joaquin Delta	X	Hatchability in nesting diving birds Health consumption advisory in effect for scaup and scoter (diving ducks)
	Suisun Bay	X	
	Carquinez Strait	X	
	San Pablo Bay	X	
	Central San Francisco Bay	X	
Lower & South Bay	Central Basin (Part of Lower Bay)	X	Health consumption advisory in effect for benthic-feeding ducks
	South San Francisco Bay	X	
	Oakland Inner Harbor – Pacific Dry Dock	X	
	San Leandro Bay	X	

While selenium concentrations in the North Bay do not exceed the National Toxics Rule chronic saltwater criterion (5 µg/L) for protection of aquatic life, the observed bioaccumulation of selenium in fish is the basis of impairment of the estuarine habitat (EST) and poses a threat to other estuarine organisms including waterfowl and shorebirds. Other designated uses of the Bay such as preservation of rare and endangered species (RARE) as well as commercial and sport fishing (COMM) are also affected by selenium. These beneficial uses are described in Table 2.

Table 2: Beneficial uses of the North Bay potentially impaired by selenium

Designated Beneficial	Description
Estuarine Habitat (EST)	Uses of water that support estuarine ecosystems, including, but not limited to, preservation or enhancement of estuarine habitats, vegetation, fish, shellfish, or wildlife (e.g., estuarine mammals, waterfowl, shorebirds), and the propagation, sustenance, and migration of estuarine organisms.
Preservation of Rare and Endangered Species	Uses of waters that support habitats necessary for the survival and successful maintenance of plant or animal species established under state and/or federal law as rare, threatened, or endangered.
Ocean, Commercial and Sport Fishing (COMM)	Uses of water for commercial or recreational collection of fish, shellfish, or other organisms in oceans, bays, and estuaries, including, but not limited to, uses involving organisms intended for human consumption or bait purposes.

2.2 Project Objectives

The proposed project is intended to evaluate the contributions of existing and future selenium discharges to the impairment of beneficial uses in the North San Francisco Bay associated with controllable water quality factors i.e. resulting from human activities that can influence water quality and be reasonably controlled through prevention, mitigation, or restoration actions. The specific goals are to:

- Reduce selenium impairment and attain water quality objectives established for the North Bay
- Protect and enhance the overall aquatic health and wildlife habitat including rare and endangered species habitat
- Protect beneficial uses of the North Bay and enhance its aesthetic and recreational values

3 BACKGROUND AND ENVIRONMENTAL CONDITIONS

3.1 Environmental Setting

San Francisco Bay, with an area of approximately 1,600 square miles, is the largest estuary on the West Coast. The region is recognized as having utmost ecological and economical importance. It supports a variety of natural habitats and a diverse wildlife population as well as provides drinking water for more than 70 percent of Californians and irrigation water for 4.5 million acres of farmland. The North Bay, in particular, supports a diverse fish biota. The fish supported include both sportfish and threatened and endangered fish species. The five most common sport fish in the North Bay are: (SFEI 2000; listed in order of catch frequency):

- Striped bass (*Morone saxatilis*)
- Halibut (*Paralichthys californicus*)
- Jacksmelt (*Atherinopsis californiensis*)
- White sturgeon (*Acipenser transmontanus*)
- White croaker (*Genyonemus lineatus*)

In addition to the sport fish listed above, the North Bay supports the following threatened and endangered fishes (Beckon and Maurer 2008):

- Chinook salmon (*Oncorhynchus tshawytscha*)
- Delta smelt (*Hypomesus transpacificus*)
- Green sturgeon (*Acipenser medirostris*)
- Longfin smelt (*Spirinchus thaleichthys*)
- Sacramento perch (*Archoplites interruptus*)
- Sacramento splittail (*Pogonichthys macrolepidotus*)
- Steelhead trout (*Oncorhynchus mykiss*)
- Tidewater goby (*Eucyclogobius newberryi*)

The Bay is commonly divided into segments including Sacramento/San Joaquin Delta, Suisun Bay, Carquinez Strait, San Pablo Bay, Central Bay, and Lower and South Bay (Figure 1). Each segment has a distinct ecological structure defined by the local tidal datum, amount of fresh water influx, sediment input, and the underlying hydrology. The North Bay extending from the Sacramento/San Joaquin Delta through Central Bay differs significantly from the South Bay as it receives almost 90% of the entire fresh water and sediment inflow into the Bay (SFEP 1992).

The northward-flowing San Joaquin and southward-flowing Sacramento Rivers discharge into the northern reach of the Bay and carry about 60 percent of the state runoff draining approximately 152,500 square kilometers or 40 percent of California's surface area (Conomos *et al*. 1985). The Sacramento River typically accounts for 80 percent of the fresh water inflow coming through the Delta into the Bay and the San Joaquin River for 15 percent. The presence of freshwater inflow into the North Bay causes stratification of Bay waters and generates horizontal salinity gradients. Salinity gradually increases from one part of salt per thousand (ppt) in the Delta to approximately 30 ppt near the mouth of the Bay (Cohen 2000). Tidal action, river flow and stratification that occur in the North Bay result in the average residence time being three to six times shorter than in the southern portion of the Bay.

Sacramento and San Joaquin Rivers are fundamental to the health and continuation of the shallow water habitats in the North Bay area; however, they also provide a conduit for selenium rich drainage and agricultural runoff. Freshwater inflows from the Central Valley watershed are the major source of new sediment input into the Bay. Most new sediment (approximately 80 percent) originates in the Sacramento - San Joaquin River drainage and enters primarily as suspended load during the high winter flows. Much of the winter sediment load initially settles out in San Pablo Bay. During the low flow summer months, wind-generated waves and tidal currents re-suspend the previously deposited sediment and redistribute it over a wider area. Selenium affiliated with sediments is effectively mobilized and could enter into food webs contributing to long-term dietary exposure of fish and wildlife (Lemly 1999). Therefore sediment dynamics exerts an important control on the distribution, transport and speciation of selenium in the Bay.

3.2 Selenium Characteristics, Speciation and Environmental Fate

Selenium is a naturally occurring trace element that is widely distributed but dispersed in the environment. It is commonly found in marine sedimentary rock formations and soils developed from parent seleniferous material.

At trace concentrations selenium is an essential nutrient for plants and animals and it is important to human health. As a vital constituent of selenoproteins, selenium plays a significant role in production of thyroid hormones, in the functioning of immune system and in prevention of oxidative stress or inflammation (Rayman 2000). However, the margin between essential concentrations of selenium in diet of plants, animals or humans and the concentrations that can cause toxicity or poisoning is the smallest among all known micronutrients.

Selenium Properties and Distribution in the Environment

Selenium has an atomic number of 34, melting point of 217°C, boiling point of 685°C, and an atomic weight of 78.96. In the periodic table it is located between non-metallic sulfur and metallic tellurium. In nature, selenium is strongly associated with sulfur. Because the radius of Se^{2-} is only slightly larger than of the S^{2-} anion selenium substitutes readily for sulfur in the structures of sulfide minerals (USGS 2004). Thus, selenium usually occurs combined with other compounds, such as in sulfide ores of other metals such as silver, copper, lead and nickel.

Average concentrations of selenium found in sediments and soils usually range from 0.01 to 0.02 mg/kg with most seleniferous soils containing less than 2 mg/kg (USDHHS 2003b, Chapter 6). However, Cretaceous and Tertiary marine and sedimentary deposits underlying and surrounding basins such as San Joaquin Valley, and those found in western states are enriched in selenium. Presser (1994) identified seleniferous deposits in the Coast Ranges of California and Central Valley with concentrations of Se reaching 45 mg/kg and median values exceeding 6.5 mg/kg.

Enrichment of selenium in soils and groundwater commonly occurs in arid and semi-arid irrigated areas where application of irrigation water accelerates weathering processes and mobilizes already elevated levels of selenium in the soil profile. To reduce effects of salinization of agricultural lands in these areas, such as the southern Central Valley, large volumes of water have to be used to flush the excess salt and selenium that accumulates in the root zone (Seiler *et al*. 2003). Drainage of irrigation excess water through the system of drains and canals is then necessary to prevent waterlogging of the soils. These drains, however, provide a conduit to carry seleniferous groundwater to surface waterbodies and wildlife areas as it was well documented in the case of disposal of agricultural drainage water into the Kesterson Wildlife Refuge. Reported selenium concentrations detected in irrigation drainage are very high and vary between 75 and 1400 µg/L (Amweg *et al.* 2003). Arid climate amplifies further evaporation related enrichment that takes place in enclosed surface waterbodies and wetlands resulting in selenium concentrations potentially reaching toxic levels.

Selenium exists in a number of chemical forms and exhibits a complex biochemistry. Most common selenium species include: elemental selenium (Se^0) selenide (Se^{2-}), selenite Se^{4+} (SeO_3^{2-}) and selenate Se^{6+} (SeO_4^{2-}). Oxidation state is the key factor determining the fate of selenium in the environment. The concentration, speciation and partitioning of selenium in a given environment are mostly govern by complex interactions between pH and redox conditions, presence of metal oxides and biological interactions (USDHHS 2003b Chapter 6). As described by Lemly (1997) the aquatic cycling of selenium includes four major pathways: 1) it can be absorbed or ingested by organisms, 2) it can bind or complex with particulate matter, 3) it can remain free in solution, and 4) it can be released to the atmosphere through volatilization.

In natural freshwater and estuarine ecosystems selenium concentrations are typically low ranging from 0.1 to 0.4 µg/L with background concentrations below 1 µg/L (Lemly 1997, Eisler 1985). Selenium concentrations in present-day seawater average approximately 0.09 µg/L (Hem 1985). Selenate and selenite are the most soluble and the most mobile forms of selenium that predominate in well-oxygenated, aerobic surface waters. Out of these two common selenium species, selenite is more readily taken up by bacteria, which, in turn, serves as a path for rapid biotransformation into organoselenides. This biologically reduced selenium, often referred to as particulate selenium, is then directly available to rooted plants, bottom-dwelling invertebrates and detrital-feeding fish and wildlife (Abu-Saba and Ogle 2005, Amweg *et al*. 2003).

Anthropogenic Sources and Uses

Despite wide distribution of selenium in the environment, deposits of selenium are not sufficiently concentrated to justify mining. Instead nearly all selenium is produced as a byproduct of the electrolytic refining of copper (SWRCB 1989). The main anthropogenic activities that may release selenium compounds to the environment include glass manufacturing, chemical and pigment manufacturing, electronics, agriculture and, pharmaceutical and nutrition industries (Table 3). The most significant emissions of atmospheric selenium result from combustion of coal and petroleum fuels (USDHHS 2003a, b). Incineration of rubber tires, paper, and municipal waste is thought to be the second largest source of atmospheric selenium.

USGS (2004) estimated that approximately 90 percent of selenium used in pigments, fertilizers, animal feeds, chemicals and pharmaceuticals dissipate into the environment. Furthermore, the content of selenium in glass and free-machining alloys is not accounted for during recycling of those materials as selenium is likely to volatilize during melting operations.

Table 3: Description of selenium sources and uses

Type of Use	Description	Estimated Se Use (%)
Glass Manufacturing	Used together with other chemical compounds to produce color glasses (black and bronze-colored architectural glass; pink, purple and yellow glass; as well as ruby glass used for lenses in traffic signal and navigation lights) Used as a decolorizer for the natural gray heat absorbent flat glass for automobile and modern office building windows Used in powdered and granulated glass applied onto the surfaces of ceramic products to seal and color them	25
Chemicals & Pigments	Catalysts and oxidizing agents in organic chemical processes Pigments used in the coloring of plastics processed and used at high temperatures, paints, enamels and rubber (e.g. for cable and steam line coverings)	22
Electronics	Photographic exposure meters and rectifiers for home entertainment equipment Plain paper xerographic copiers (selenium is used to coat metal cylinders from which a photographic image is transferred). Selenium is gradually being replaced in copiers by silicon and other materials Solar photocells	10
Metal Manufacturing	An additive to improve machinability of copper, lead and steel alloys	24
Other	Catalyst in preparation of various pharmaceuticals Feed additive for poultry and stock Dietary supplement Cosmetics (Antidandruff shampoos)	19

Compiled from USGS (2004)

3.3 Ambient Selenium Levels in the North Bay

Concentrations of selenium in the North Bay water column and bottom sediments have been monitored since the 1980s. Early on the monitoring effort focused on the northern segments of the Bay because sub-surface drainage of agricultural areas in the San Joaquin Valley and waste streams from oil refineries in the Suisun Bay and Carquinez Strait conveyed large amounts of selenium to the Bay. Regional Monitoring Program (RMP) and the data collected by Dr. Greg Cutter's research group at Old Dominion University[1] are the two most comprehensive sources of selenium data in the North Bay. Sampling design, frequency and

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[1] Funded by the U.S. Bureau of Reclamation, CALFED (Grant 01WRPA0077), California DWR, and National Science Foundation, Environmental Geochemistry and Biogeochemistry Initiative (Grant: OCE-9707946).

quality assurance procedures are described in detail in SFEI (2006), Cutter and Cutter (2004) and Doblin *et al*. (2006). General sampling locations are shown in Figure 2. Technical Memorandum No. 2 prepared by Tetra Tech (2008a) provides a summary of all the available data and describes spatial and temporal changes in water and sediment quality.

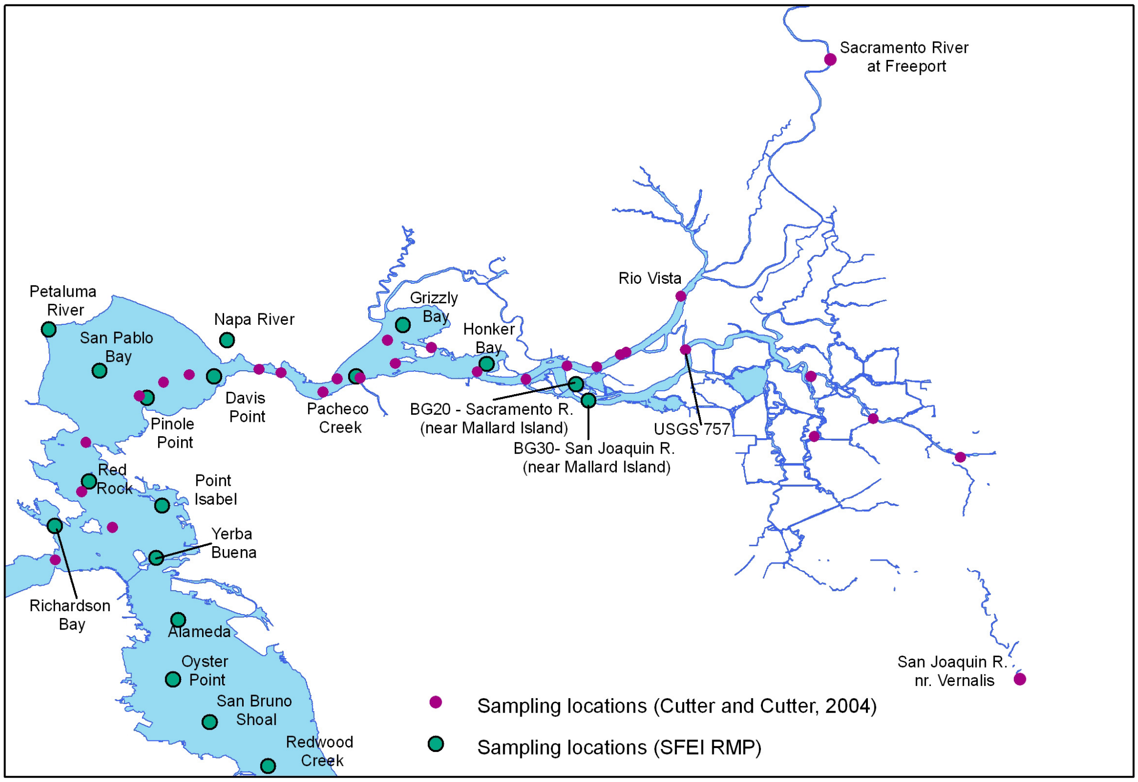

Figure 2: Locations of RMP long-term monitoring sites and sampling by Cutter and Cutter (2004) during November 1999 *(Tetra Tech 2008a)*

The ambient total selenium levels in the North Bay measured between 1993 and 2005 are consistently low and do not exceed 0.5 µg/L. The mean dissolved and total selenium concentrations at each monitoring location range from 0.12 to 0.18 µg/L and 0.13 to 0.24 µg/L respectively. Dissolved selenium is the predominant form present in the water column. Particulate selenium, calculated as a difference between total and dissolved selenium, accounts for approximately 10% of the total selenium. The most recent data collected during 1999-2005, i.e., following the improved wastewater control measures implemented by the oil refineries in 1999, indicate a slight decrease in concentrations of dissolved and total selenium at 0.10 µg/L (n = 105) and 0.13 µg/L (n = 100). In comparison, mean dissolved and total selenium concentrations for the period of 1993-1999 at the same monitoring locations were 0.17 µg/L (n = 258) and 0.20 µg/L (n = 230).

Spatially, total selenium concentrations are marginally higher in the mid-estuarine regions of Suisun and San Pablo Bays when compared to the freshwater and marine portions of the estuary (Figure 3). Total selenium concentrations in the Central Bay are lower, most likely due to ocean exchange and dilution. A few locations near the confluence of local tributaries (e.g., Petaluma and Napa River) show higher total selenium than the rest of the Bay.

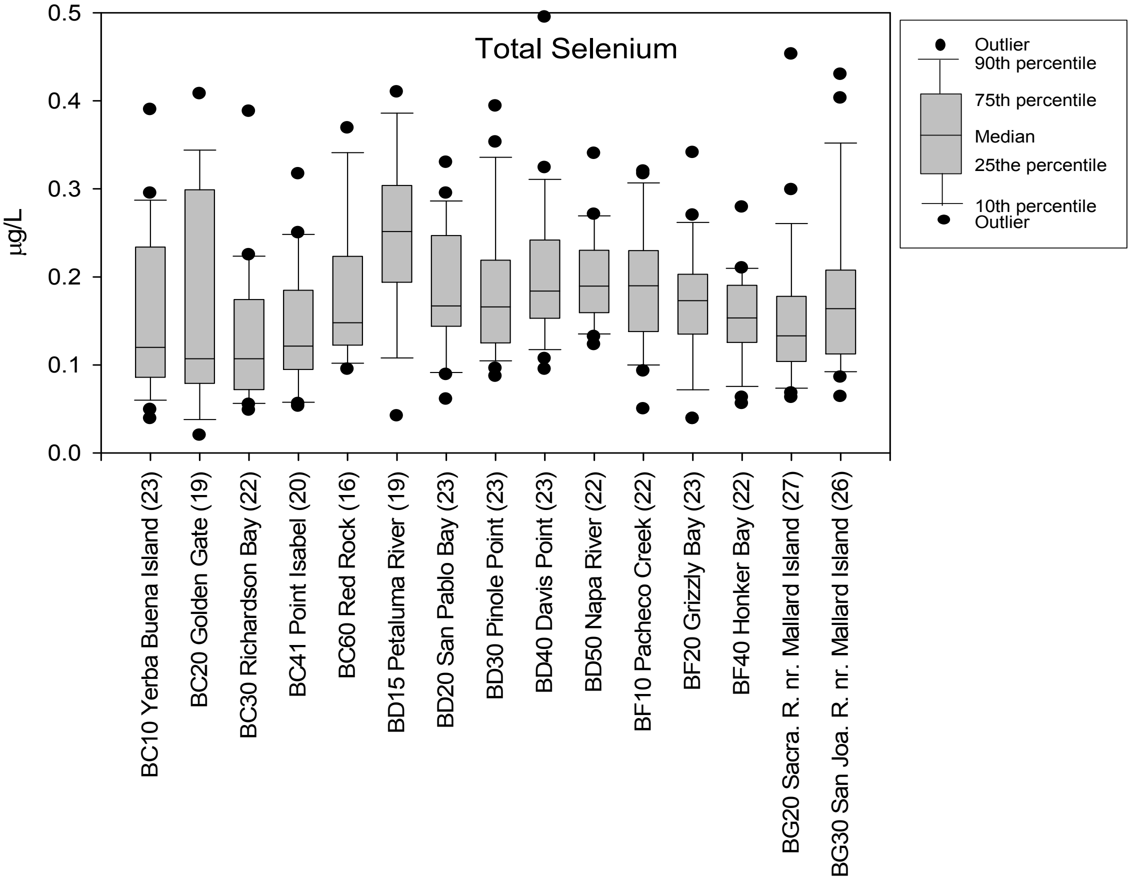

Figure 3: Total selenium concentrations at long-term RMP monitoring sites for the period of 1993-2005 (*Tetra Tech 2008a*)

Values in parentheses are numbers of samples *(Data: RMP)*.

Figure 4 shows selenium speciation in the North Bay and at the downstream reaches of the Sacramento and San Joaquin Rivers where they enter the Delta. The composition of selenium species in the North Bay is markedly different to that observed in the Delta. In the Bay water column selenate is the dominant form and averages above 50% of total selenium. However, a relatively high proportion of organic selenide and selenite is still present, accounting for approximately 20% each. In the freshwater flows from Sacramento and San Joaquin Rivers selenate concentrations account for more than 70% of total selenium with the remainder equally distributed between selenite and organic selenide.

The changes in selenium composition resulting from the improvements in the wastewater treatment at the refineries are clearly visible during low flow conditions surveyed in 1986 and 1999. In 1986, the selenite fraction of total selenium exceeded 35% and almost matched selenate. Since then, selenite concentration decreased significantly and it now accounts for approximately 15% of total dissolved selenium during low flow.

Over the long-term, dissolved and total selenium concentrations show temporal variations, both inter-annual and seasonal but the overall selenium levels remain low in the North Bay. The temporal patterns in dissolved selenium closely resemble those in the total selenium. Data from the RMP random sampling period of 2002-2008, indicated that dissolved and total selenium concentrations were usually below 0.15 µg/L, with an average for the entire North Bay of 0.10 µg/L. Total selenium concentrations are higher in the upper estuary (Suisun Bay) than in the San Pablo and Central Bays.

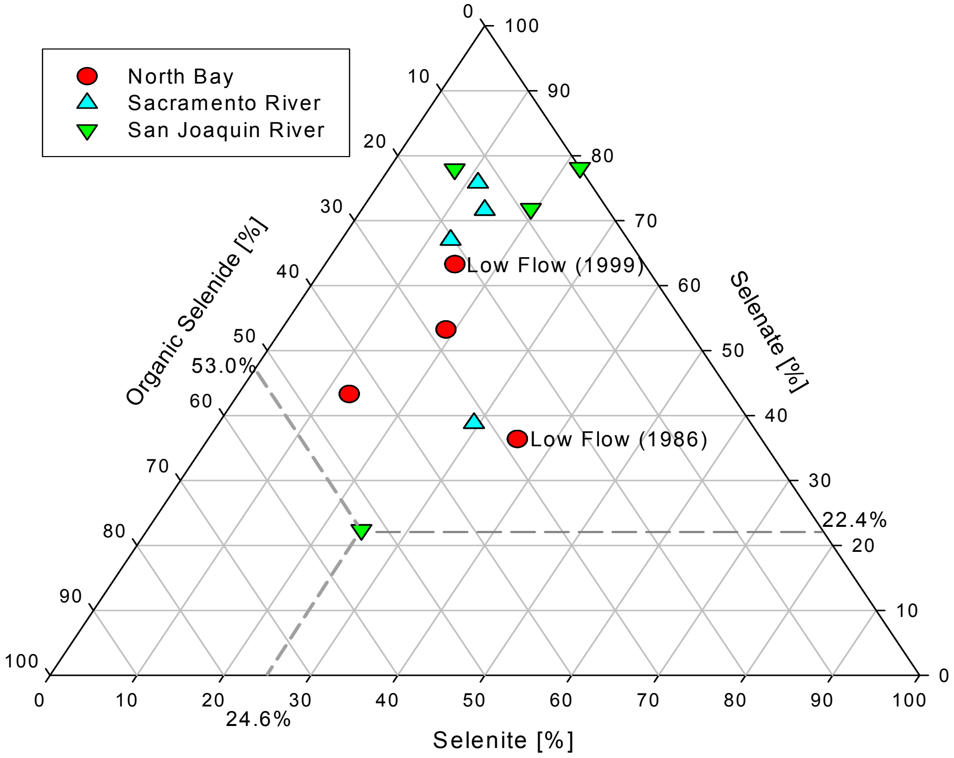

Figure 4: Speciation of dissolved selenium in North Bay and main tributaries
(Data: Cutter and Cutter 2004)

Although most selenium in the water column at any given time is in one of the dissolved forms, the suspended particulate material still comprises 2 to18.5% of the total selenium. This particulate selenium is also more readily available to bivalves and zooplankton. Suspended materials in the North Bay waters include mineral particles, particulate organic matter (non-living), and living organic matters, primarily algae and bacteria. These suspended particles may originate from the various non-point sources discharging to the Bay, may be generated in situ, or may be eroding from the sediment bed. Studies indicate that particulate selenium is a function of phytoplankton productivity and riverine inputs of sediment to the Bay (Abu-Saba and Ogle 2005). In general, particulate elemental selenium is associated with bed sediments while particulate organic selenium is associated with algal/bacterial uptake, and selenite and selenate are sorbed to mineral particles and/or particulate organic matter.

Doblin *et al*. (2006) reported concentrations of total suspended particulate material (TSM) and selenium on particles in San Francisco Bay for the time period from 1997-1999. Particulate selenium concentrations, including elemental selenium and particulate selenate and selenite, generally track the pattern in total suspended material and decrease along the salinity gradient especially during high flow conditions (Figure 5), and are usually lower during high flow than low flow. However, the levels of organic selenium remain similar during low and high flow periods and even increase with travel distance in the estuary, indicating that biotransformation of selenium may occur in the estuary where more oxidized forms of selenium (likely selenite) are incorporated into a wide variety of organic compounds.

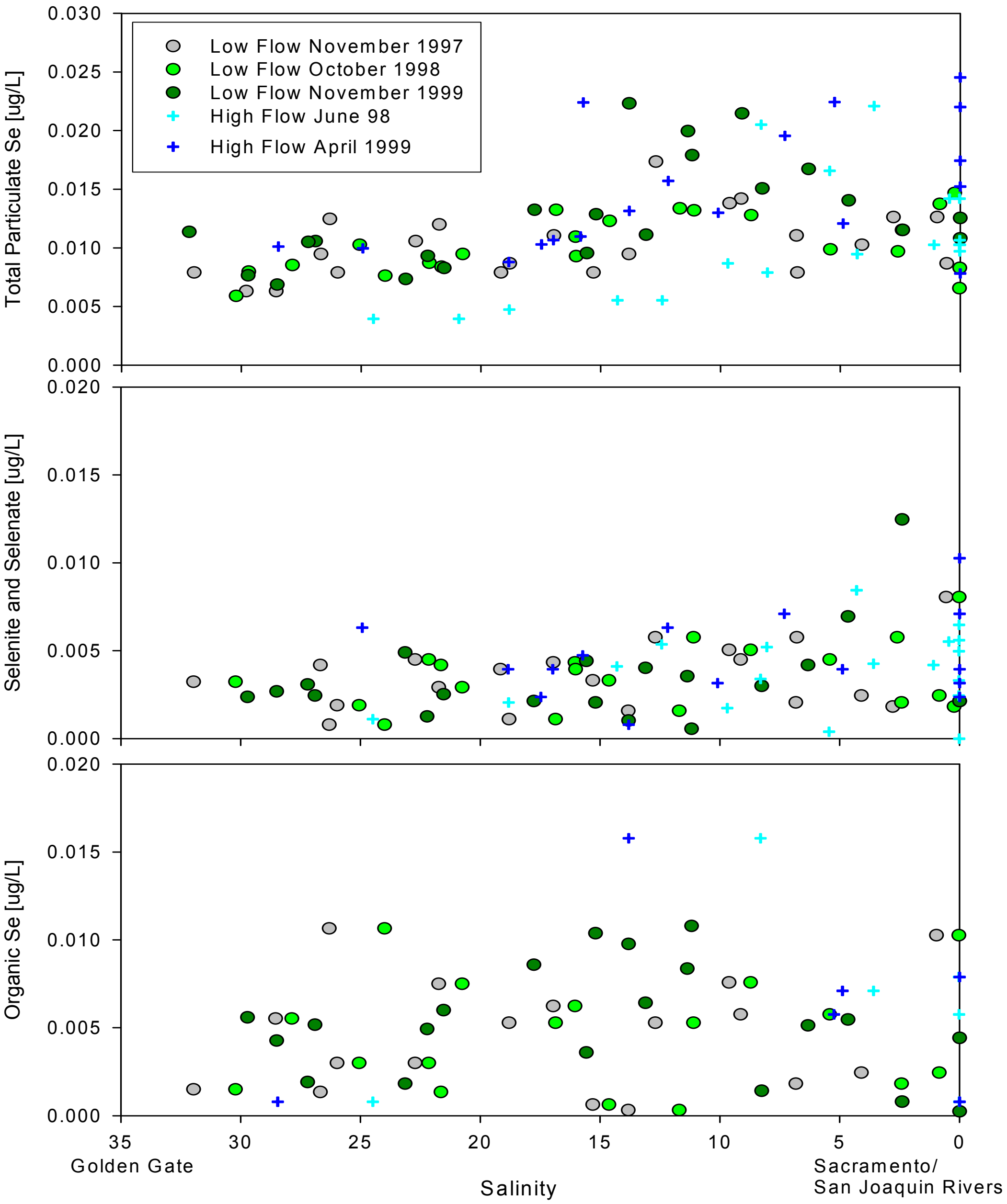

Figure 5: Distribution of particulate selenium along the salinity gradient during different flow conditions *(Data: Doblin et al. 2006)*

4 NUMERIC TARGETS

Numeric targets identify specific water column, sediment and/or tissue indicators that express the desired conditions of the water body and ensure attainment of the water quality standards including water quality objectives and beneficial uses. TMDL targets are often set to applicable numeric water quality objectives. However, the existing water column based criteria may not ensure adequate protection of aquatic organisms in the North Bay. Despite very low ambient selenium levels in the water column, concentrations in some fish tissue samples exceed ecological risk guidelines (Presser *et al*. 2004), which form the basis of the impairment in the Bay. Therefore, we propose a sturgeon-based fish tissue numeric target as the most direct way to address selenium impairment and assess protection of beneficial uses (Table 4).

Table 4: Proposed numeric target for selenium in the North San Francisco Bay

TMDL- North Bay	**Fish Tissue µg/g – dw**
Numeric target	6 - 8.1

The proposed target aims at protection of white sturgeon, the fish that is particularly vulnerable to selenium exposure in the North Bay. Sturgeons are long-lived fish found year-round in the Bay with a high propensity to bioaccumulate selenium because of their feeding preferences and reproductive biology. They feed predominantly on benthic organisms including the invasive clam, *Corbula amurensis,* which is very efficient in accumulating and retaining selenium. Sturgeon exposure is further exacerbated by its long reproductive cycle during which selenium is transferred and stored in developing eggs, forming a stable selenium reservoir in reproductive females.

The selected target is set to the range of values that the USEPA is considering as wildlife criterion for San Francisco Bay/California (D. Fleck, USEPA, *pers. comm.*) and is based on an estimate of the concentrations at which an effect is observed in 5% (EC5) to 10% (EC10) of the population. The tissue concentration within this range is deemed to be sufficiently protective of the most sensitive fish species that reside in San Francisco Bay. The USEPA has not yet offered the scientific rationale for recommending a specific value. Therefore, in this Chapter, we provide a scientific context for establishing a numeric target for the TMDL, an overview of the selenium toxicity relevant to fish and birds in the North Bay, and the applicable existing objectives and health and risk criteria, which equate to attainment of water quality standards.

4.1 Selenium Bioaccumulation and Impact on Aquatic Life

Evidence of fish and wildlife contamination, leading to reduced survival and deformities due to selenium in aquatic and terrestrial food webs, has been documented extensively (Hamilton 2004, Fan *et al*. 2002, Skorupa 1998). These studies confirmed that once selenium enters the aquatic environment it has a high potential to bioaccumulate in zooplankton and benthic invertebrates, and, subsequently, to biomagnify as it reaches top level predators such as fish, birds and mammals.

Bioaccumulation describes selenium's tendency to be taken up from the environment and stored at increased concentrations by organisms. The rate of bioaccumulation is often site-specific and highly dependent on the selenium forms present, the environmental conditions and the type of the organism. In San Francisco Bay, selenium uptake and bioaccumulation effects are particularly evident in the dominant estuarine clam *Corbula amurensis* (Schlekat *et al*. 2004, Linville *et al*. 2002). The studies found that this clam displayed a 10-fold slower rate constant for selenium loss compared to common crustaceans, such as copepods and mysids, leading to increased bioaccumulation of selenium. In 1995-1997 Se concentrations in *C. amurensis* found in the North Bay varied seasonally from 5 to 20 µg/g dry weight (dw). These concentrations are within the range of values that are linked to a high frequency of developmental toxicity in wildfowl based on diets of more than 8 µg/g dw and teratogenic effects observed in fish at dietary selenium concentrations above 5 µg/g dw (Schlekat *et al.* 2004). In addition, stable isotope analyses used by Stewart *at al*. (2004) revealed that bottom feeding fish (e.g. white sturgeon and splittail) exhibited isotope signatures indicative of diets that included bivalves and therefore could be under greater risk from selenium.

Biomagnification occurs where there is a progressive buildup of selenium in organism at higher trophic levels. Figure 6 depicts conceptually how selenium biomagnifies in the tissues of organisms present in San Francisco Bay. Lemly (1997) reported that biomagnification might lead to a two to six-fold increase in selenium concentrations between primary producers and forage fish. This, in turn, may have detrimental effects on fish and waterfowl even when selenium in the water column is present at low concentrations.

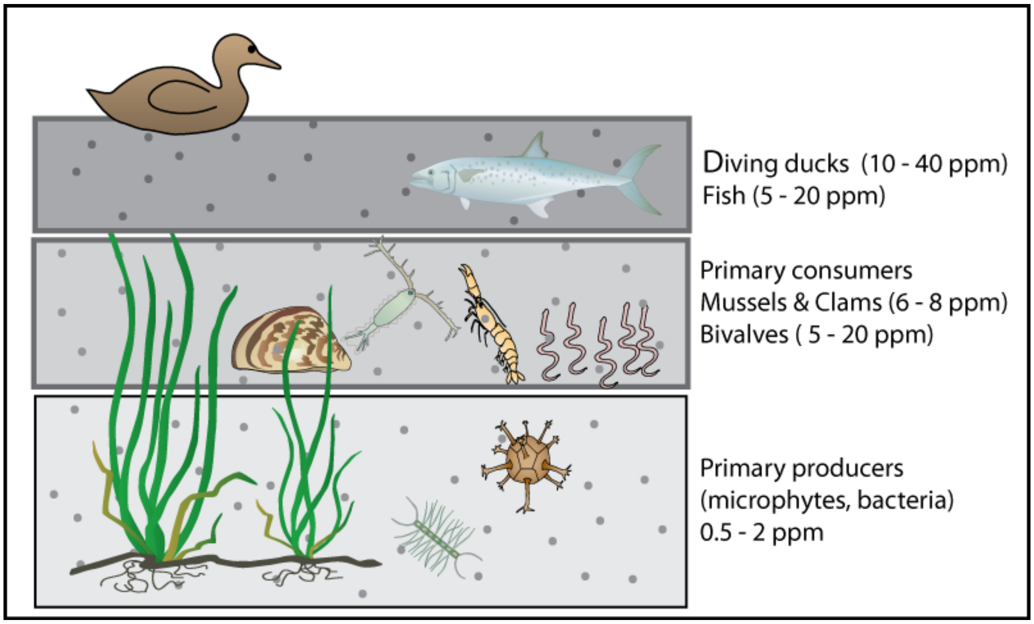

Figure 6: Conceptual representation of selenium biomagnification in the North Bay
(Concentrations illustrate the range of selenium found in the North Bay species. Concentrations are measured as total selenium in tissue and expressed as micrograms per gram (ppm) dry weight)

4.2 Toxicity and Selenium Related Risks

Aquatic and terrestrial organisms are highly sensitive to selenium contamination. They require 0.5 µg/g dw of selenium in their diet to sustain metabolic processes, however, concentrations that are only an order of magnitude greater than the required level have been shown to be toxic to fish (USEPA 2004). The main toxicological effects in fish and aquatic birds involve reproductive abnormalities, teratogenic deformities, selective bioaccumulation, and growth retardation (Eisler 1985).

Toxicity of selenium to wildlife has been researched for many years and numerous studies have documented that, in contrast to many other microelements, chronic toxicity resulting from dietary and food chain exposure causes a much greater problem than toxicity associated with water exposure (for example see: Lemly 1997, Canton and Van Derveer 1997, Hamilton 2002). Reproductive effects in fish and aquatic birds have been identified as the most sensitive biological indicators of aquatic ecosystem-level impacts of selenium.

This section summarizes the available information on the toxicity of selenium to fish and birds and reviews concentrations associated with toxic effects to help establish the numeric target. The discussion of selenium toxicity takes into account the studies and methods described in the *North San Francisco Bay Toxicological Assessment* (2008b) prepared by Tetra Tech Inc. and refers to the review of existing selenium dietary exposure benchmarks by Beckon and Maurer (2008). The toxicity-based screening values have been derived from the available scientific literature that considered either dietary or dietary and waterborne selenium exposures.

Evaluation Methods

Eighty fish toxicity studies reported from 1987 to 2007 were identified and evaluated using a set of predefined exclusion and acceptability criteria (Tetra Tech 2008b). The reported effects from each study that met the initial criteria were grouped into one of two categories: major and minor effects. Major effects are those that have the potential to impact fish or birds at the organism and/or population level (e.g., increased mortality, reduced fecundity, reduced growth). The lowest observed adverse effect levels (LOAELs), effect thresholds, species mean chronic values (SMCV), effect concentration (EC01 or EC10) and species sensitivity distributions (e.g. Hamilton 2003, 2004) were then used in the derivation of proposed screening values.

When there is a large body of literature, with many reported LOAELs, the lowest observed adverse effect level is likely to be indicative of the concentration at which effects first appear. However, when there are only a few studies, which is often the case in this assessment, it is likely that effects begin at a level below the lowest LOAEL reported. Effect thresholds are calculated as the geometric mean of the no observed adverse effect level (NOAEL) and LOAEL reported for the same effect in an individual study. Since toxicity tests do not generally test many different concentrations, and effects may occur at concentrations below the LOAEL, calculating the geometric mean of the NOAEL and the LOAEL is a way to add a margin of safety to the LOAEL. A similar approach is recommended for establishing risk-based ecological soil screening levels (USEPA 2005) and for developing water quality criteria (USEPA 1985).

To provide a better comparison between toxicity effects reported by different studies, tissue concentrations expressed as wet-weight values were converted to dry-weight values and, similarly, if not reported, the whole-body concentrations were calculated using the USEPA methods (USEPA 2004). The USEPA recommends the whole-body tissue based medium as the best means of expressing the chronic criterion value because of the general availability of the data and practicality of performing the tests.

After applying the screening criteria, 19 studies with usable toxicity data were identified as suitable for derivation and comparison of the screening levels for fish and 23 studies for birds. The studies reported toxic effects associated with dietary or dietary and waterborne exposure for six species of fish: bluegill, fathead minnow, rainbow trout, Chinook salmon, Sacramento splittail and white sturgeon. All experiments, with the exception of one involving Chinook salmon, were conducted in freshwater.

Selenium Toxicity Thresholds in Fish

The available selenium toxicity data showed a broad range of sensitivity among tested fish and included observed threshold effects at very low concentration levels suggesting that the dataset provides a good approximation of the expected effects that are applicable to most fish species (Figure 7). The larvae of rainbow trout exhibited the most sensitivity to Se toxicity with the whole-body LOAEL concentration of 2.3 μg/g-dw for the growth endpoints. The lowest species mean chronic value (SMCV) of 3.0 μg/g-dw was estimated for channel catfish followed by the bluegill and fathead minnow with SMCVs of 5.6 and 6.0 μg/g-dw. However, the North San Francisco Bay does not support these freshwater fish species nor were they considered at risk specifically for selenium toxic effects in the Bay/Delta estuary in the Beckon and Maurer (2008) review.

Sacramento splittail and sturgeon

The effect thresholds and LOAELs for juvenile Sacramento splittail and white sturgeon, the two important species of concern in the North Bay, are above 6 and 10 μg/g-dw respectively (Figure 7). These estimated screening levels correspond well with thresholds for reproductive toxicity in fish (Beckon and Maurer 2008).

Both, the Sacramento splittail and white sturgeon, feed primarily on benthic organisms including introduced bivalves that have been proven to be very proficient selenium bioaccumulators. This in turn may lead to a greater potential for selenium toxicity for these fish. Clams and other mollusks were found to predominate the stomach contents of white sturgeon caught by anglers in Suisun Bay (1965-1967), reaching up to 77% of stomach volume. The diet of the splittail collected in Suisun Marsh was dominated by detritus with the proportion of bivalves increasing markedly after the decline of Mysid shrimp in the San Francisco Estuary (Feyrer *et al.* 2003).

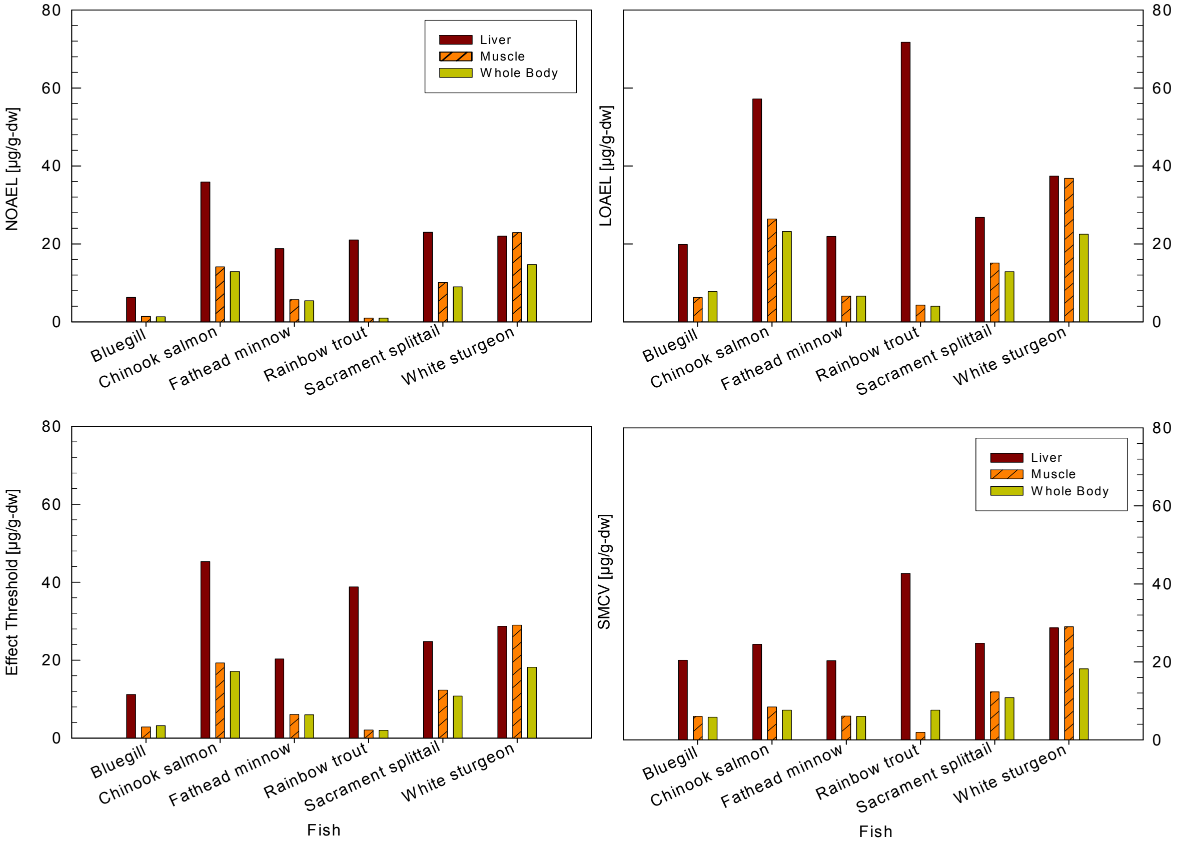

Figure 7: Selenium concentrations in selected fish at which adverse effects may occur

(Figure compiled from the data presented in Table 3-3 (Tetra Tech 2008b)
showing the most stringent toxicity levels from studies of juvenile fish)

Despite the diet comprising primarily bivalves, splittail tissue collected in 2000 from Suisun Slough (USGS, unpublished data) did not show elevated levels of selenium. In fact, the observed muscle concentrations in juvenile fish varied from 1.5 to 3.5 µg/g-dw, and in adult fish from 1.5 to 4.1 µg/g-dw, and were well below known toxicity thresholds. These concentrations are also indicative of background level diets not exceeding 1 µg Se /g. Deng and others (2007) observed relatively slow selenium depletion in the muscle of splittail fed a 12.6 µg/g diet for 9 months that was then followed by 21 weeks of a control diet of 0.4 µg/g. At the end of the experiment the measured concentrations ranged from 11 to 13 µg/g in fish exposed to higher dietary selenium and remained constant at approximately 3 µg/g in fish fed the control diet for the entire experiment. Furthermore, faster elimination rates were detected at the end of a 21-week depuration in fish previously exposed to very high dietary selenium (26.0 and 57.6 µg/g) that might indicate the ability of splittail to cope with the short-term exposure without adverse effects. The authors concluded that based on the observed growth, tissue accumulation and histopathology, splittail that survived the 9-month exposure to 12.6 µg/g or less could thrive under normal dietary exposure.

One explanation for low tissue concentrations in the North Bay could be related to the fact that splittail may not be consuming Asian clam for several months each year. This fish is known to spawn in inundated terrestrial vegetation in the upper Estuary and their recruitment is strongly associated with the magnitude and duration of floodplain inundation during wet season winter months when the clam population usually experiences a notable decline (Deng *et al.* 2007, Parchaso and Thompson 2002). During laboratory experiments Teh and others (2004) determined that at least 9 months of chronic exposure to a diet of 6.6 µg/g was necessary to induce possible deleterious health effects and these conditions are unlikely to occur in the part of the estuary frequented by splittail.

The relatively high selenium concentrations exceeding 10 µg/g-dw found in the muscle of white sturgeon collected by the RMP from San Pablo Bay between 1997 and 2006, might be linked to a diet composed of bivalves and in particular the Asian clam. Even higher concentrations exceeding 30 µg/g-dw were measured in adult sturgeon caught near Pittsburg in 2000-2001 (USGS data). However, Linares and others (2004) reported selenium in 39 sub-adult sturgeon caught between 2002 and 2004 at levels below 11.9 µg/g-dw with an overall mean concentration of 6.59 ± 0.45 µg/g-dw.

Linville (2006) observed similarly high but greatly variable selenium concentrations in the experimental study with white sturgeon fed with mostly seleno-methionine diets of 15 to 45 µg/g and concluded that the laboratory results were consistent with the conditions in San Francisco Bay-Delta where the Asian clam was also a common food source for white sturgeon. Despite the high variability in observed selenium bioaccumulation rates Tashijan *et al*. (2006) suggested that juvenile white sturgeon are relatively less sensitive to selenium toxicity than other fish species and even the dietary concentrations exceeding 190 µg/g-dw did not affect the survival of sturgeon (the mean survival rate was 99±0.43%). This study also determined on the basis of frequency of kidney lesions, that the adverse effects occurred when white sturgeon were fed 20.5 µg Se /g in the diet. When all sensitive endpoints were considered, no effects were observed with a diet of 9.6 µg Se /g. The corresponding whole-body tissue concentrations with sturgeon fed these diets were 14.7 µg/g-dw (LOAEL) and 11.8 µg/g-dw (NOAEL) respectively.

However, certain developmental defects such as edema and skeletal deformities could occur at lower tissue concentrations (B. Beckon, US FWS, *pers. comm.*). The experimental results reported in the above two studies indicate that these effects begin to get significant when the EC10 exceeds 8.13 μg/g dw (Figure 8).

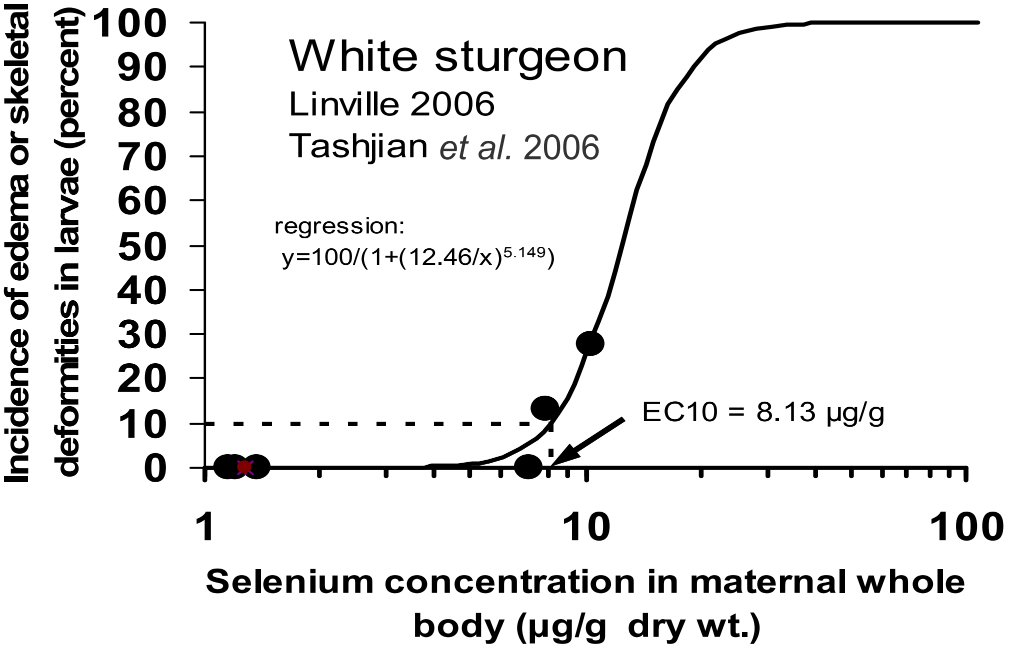

Figure 8: Relationship between selenium in the whole bodies of adult female white sturgeon and the occurrence of edema and/or skeletal deformities in the larvae that hatch from their eggs.

(data from Linville 2006 and Tashjian *et al.* 2006, converted from muscle Se concentrations to whole body concentrations, after Beckon, *pers. comm.*)

Compared to white sturgeon, very little direct information is available for the threatened green sturgeon. In one study that tested the green and white sturgeon response to changed environmental conditions, Kaufman *et al*. (2008) concluded that green sturgeon exhibited much greater sensitivity to selenium. The noticeable declines in predator avoidance and reduced swimming performance in green sturgeon were detected at the dietary dose of 20 μg SeMet/g. However, selenium concentrations and dose spacing used in the experiment were too high to be applicable to the conditions in the North Bay and to accurately determine the toxicologically significant thresholds. In general, white sturgeon is considered to be a representative surrogate species for the green sturgeon (Beckon and Maurer 2008, D. Fleck USEPA *pers. comm.*, April 28, 2010).

The protection of the green sturgeon using a numeric target developed based on the white sturgeon data is supported by the habitat and life history of the two species. Green sturgeon are the most anadromous of the sturgeon species and adults and sub-adults spend a large portion of their lives in coastal marine waters outside of the estuary. Typically green sturgeon use the San Francisco Bay during their infrequent (every 2 to 4 years) spawning migrations up to 240 miles upstream the Sacramento River. Juveniles may rear in freshwater and then estuarine waters for 1 to 4 years before dispersing into salt water (73 Federal Register 52084 52110, Sept 8, 2008). Data for white sturgeon indicate that young fish appear to have low selenium levels in spite of spending prolonged periods of time in the estuary (Linares *et al.* 2004).

Chinook salmon

In contrast to sturgeon and splittail, the diet of young Chinook salmon in the Delta consists primarily of insects and crustacean potentially resulting in lesser exposure to selenium. Hamilton *et al*. (1990) conducted a growth and survival study with Chinook salmon in standardized freshwater and brackish water during which swim-up larvae were fed one of two different diets. The survival rate of 94.1 to 95% was observed in larvae exposed for 60 days to seleno-methionine diet at concentrations of 9.6 and 5.3 µg/g-dw, respectively. At the higher (95%) survival rate the selenium concentration in tissue of the tested fish was 3.1 µg/g-dw with the mean larval weight just marginally less than the weight of fish with tissue concentration of 0.9 µg/g-dw and selenium diet of 1 µg/g-dw. The residence time of Chinook salmon juveniles in the estuary was also estimated to range from a maximum of 64 (Beckon and Maurer 2008) to less than 40 days (MacFarlane and Norton 2002), which corresponds to the exposure time used in the experiments that did not result in any significant adverse effects.

The calculated whole body effect thresholds based on the results from the study by Hamilton *et al*. (1990) are 7.6 µg/g-dw for freshwater and 17.1 µg/g-dw for brackish water. These calculations exclude the results of the experiments in which larvae were fed field-collected mosquitofish, from San Luis Drain thought to be potentially contaminated by pesticides and heavy metals. These effect thresholds were higher than those established for bluegill and catfish. This is contrary to the findings reported by Beckon (2007), who employed a biphasic model to all the data from the study by Hamilton *et al*. (1990), and estimated that 20% mortality may occur in Chinook salmon with tissue concentration in excess of 2.5 µg/g-dw. The optimum selenium concentration in that interpretation was assumed to be approximately 1 µg/g whole body-dw. This concentration is lower than the natural background concentrations found in fish from areas where selenium is attributed to natural geologic sources (Eisler 1985).

The results of a stochastic population model simulating the chronic level exposure in cutthroat trout which have similar early life-stage characteristics to those of rainbow trout or Chinook salmon also confirm that adverse effects from selenium occur at somewhat higher concentrations. Van Kirk and Hill (2007) simulated the conditions in the upper Snake River basin and showed that resident cutthroat trout populations were more sensitive to selenium contamination than migratory populations. Based on the modeling results the authors recommended 7 µg/g-dw as the maximum allowable concentration in whole-body fish tissue to protect cutthroat trout.

Salmonids in the North Bay are potentially among the most sensitive species of fish; however, their migratory nature, the length of time they spend in the estuary and their predominant diet of insects and crustacean imply that these fishes are at lesser risk from selenium than sturgeon or Sacramento splittail.

Toxicity Mitigating Conditions

Environmental factors and water quality parameters have been used in developing the aquatic life criteria for toxic pollutants in recognition of their mitigating effects, and to account for the site-specific conditions in a particular water body. Sulfate content and salinity are among the factors that have been shown to potentially alleviate selenium related toxicity to aquatic organisms. Antagonistic effects from sulfate content on either uptake or acute toxicity of selenate have been reported for algae, aquatic invertebrates, Chinook salmon and fathead minnows (USEPA 2004).

Hansen *et al*. (1993) demonstrated that sulfate concentrations significantly reduced the accumulation of selenium in two aquatic invertebrates: *Chironomus decorus* and *Daphnia magna*. Based on the results of the laboratory experiments the study concluded that although increased levels of sulfate could not totally prevent selenate absorption, over 40% reduction in tissue selenium concentrations was observed in both invertebrates for the Se to S ratios between 1:0 to 1:480. Similarly, juvenile rainbow trout acclimated in high salinity water (16.8 dS/m) prior to dietary exposure were more resistant to 180 µg/g dietary seleno-methionine treatment and experienced limited mortality (33 and 0%) compared to tests in freshwater where 100% mortality occurred (Schlenk *et al.* 2003). This reduction in selenium uptake has been attributed to salinity and the presence of sulfate ions that may prevent the interaction of seleno-methionine with proteins on subcellular level.

Hamilton and Buhl (1990) conducted 24-hr and 96-hr acute toxicity tests with advanced fry of Chinook salmon and coho salmon in fresh and brackish waters simulating the conditions in the San Louis Drain. Although the study focused on examining the impact of multiple contaminants and the sensitivity of various life stages of fish, the reported acute toxicity to selenate and selenite expressed as LC50s were consistently higher in the standardized brackish water compared to tests in freshwater. In addition, the authors estimated the margin of safety from the pooled LC50 data for Chinook salmon expressed as a difference between selenium levels resulting in no effects and toxic effects. The margin of safety for both selenate and selenite was significantly higher in brackish water with the value for more toxic selenite estimated at 276 in freshwater and 468 in brackish water. Similarly, in a chronic toxicity study with fingerlings size Chinook salmon exposed to dietary selenium for 120 days, the fish survival was significantly reduced in freshwater but not affected in brackish water (Hamilton *et al.* 1990). In a 10-day seawater challenge test that followed the dietary exposure, the fish survival was significantly reduced but only in fish fed in excess of 35 µg Se/g. Evidence of no effects on growth or survival in fish fed 26 µg Se/g prior to a 3-month seawater challenge was also provided.

Even though the data are limited, fish seems to exhibit much higher resilience to selenium toxicity in saltwater with higher sulfate content than freshwater. The results of these studies suggest that levels of sulfate occurring in the North Bay are likely to provide added level of protection against selenium toxicity and at the same time account for an implicit margin of safety in our review of the screening values for fish.

Selenium Toxicity Thresholds in Birds

Selenium toxicity in birds has been recognized as an issue of concern since the 1980s (Ohlendorf and Fleming 1988, Skorupa 1998).This evaluation of selenium toxicity focuses on six bird species that have been identified by Beckon and Maurer (2008) to be the most at risk from selenium and are common in the San Francisco Bay/Delta area. These species include black scoter, California clapper rail, greater and lesser scaup, surf scoter and white-winged scoter and are considered to be exposed to selenium because of their main feeding habits and/or wintering locations. Although San Francisco Bay is described as an important habitat and wintering area for waterfowl, no direct toxicity information is available for any of the birds species listed above. Instead, this section of the report summarizes the available information on avian toxicity in general and examines toxic concentrations in the diet and eggs of typical laboratory test species.

The dietary screening levels reflecting potential adverse effects for bird species in the North Bay were determined based on a review of more than 40 selenium toxicity studies. Chickens and mallards were the bird species for which most information was available. The dietary toxicity data showed a similar broad range of sensitivities and variability as presented for fish (Figure 9).

The evaluation of toxicity studies confirmed that reproductive success, such as egg hatchability, egg fertility and chick survival was the most sensitive endpoint in the tested birds, especially in mallards. In addition, the results for chickens indicated the growth/survival was also one of the sensitive endpoints. A large variability in the effect threshold ranging from 1.5 to 17.3 may suggest that these birds have potentially greater resilience to selenium toxicity. Similarly, immature mallards seem to be able to tolerate relatively high selenium concentrations reaching 17 µg/g-dw without experiencing adverse effects (Heinz *et al.* 1990).

Since no toxicity data on bird species of concern in the North Bay are available, data from the available bird studies were used and allometric scaling applied to better estimate the pertinent risk levels (Tetra Tech 2008b). In ecological risk assessment, allometric scaling is often used to extrapolate toxic responses observed in avian test species to the wildlife endpoint species of interest (Sample and Arenal 1999). The allometrically adjusted toxicity values account for differences in body weight, metabolism, pharmacokinetics and sensitivity to allow for the best available estimate of species-specific toxicity when data are lacking.

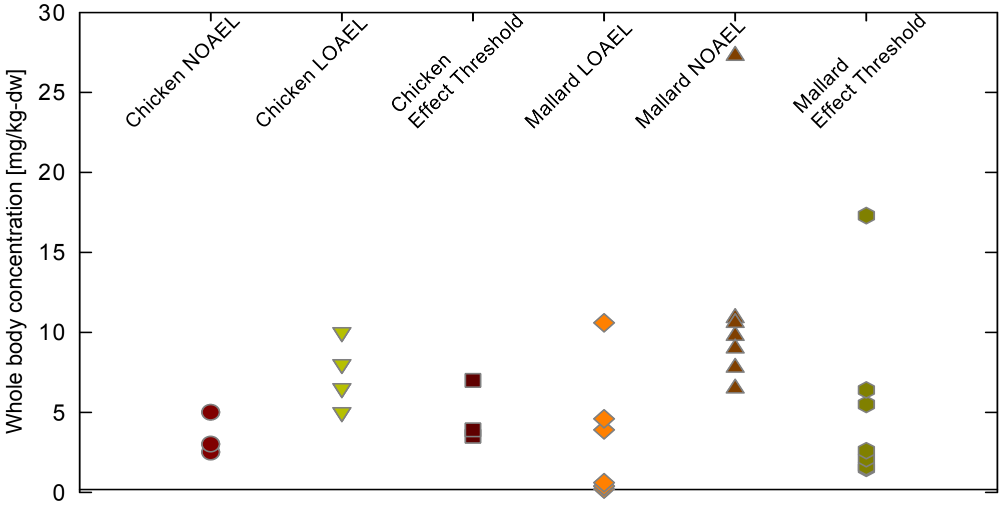

Figure 9: Observed range of dietary selenium concentrations at which adverse effects in birds may occur

In an effort to relate the known toxicity levels observed in chickens and mallards to the species of concern in the North Bay the allometrically adjusted toxicity values were calculated using the following equation:

$$TRV_a = TRV_t \left(\frac{BW_t}{BW_a} \right)^{(1-b)}$$

where:

TRV_a - allometrically adjusted toxicity value

TRV_t - toxicity reference for a test species

BW_t and BW_a - body weights (in kg) for the test and wildlife species, respectively, and

b - allometric scaling factor (this factor is not specific to Se but is a mean value for other contaminants)

The available dietary toxicity values considered as the most indicative of reproductive success were used in the calculation of allometrically adjusted screening values for birds in the North Bay. The calculated results in Table 5 show large variations depending on the type of the original test species and the toxicity thresholds used. The adjustment based on the studies for mallard ducks that share many common characteristics with most birds of concern in the North Bay indicates that clapper rail could be sensitive to dietary Se concentration of 2.2 µg/g-dw and that diving ducks (scaups and scoters) show fairly consistent sensitivity threshold within a range of 3.2 to 5.6 µg/g-dw (mean 4.1).

Table 5: Allometrically adjusted dietary selenium screening values for birds in the North Bay

Bird Species	Dietary Screening Value [µg/g-dw]	
	Mallard [a]	**Chicken** [b]
California clapper rail	2.2	0.9
Greater scaup	3.9	1.6
Lesser scaup	3.2	1.3
White-winged scoter	5.6	2.3
Surf scoter	4.1	1.7
Black scoter	3.9	1.6

a – EC10 for reduced hatching success from Adams *et al*. (2003) and Ohlendorf (2007) of 4.4 µg/g-dw

b – effect threshold for reduced hatching success of 3.9 µg/g-dw from Ort and Latshaw (1978)

Clapper rail

Although clapper rail depends on a diet that includes benthic invertebrates, these birds feed predominantly on plaited horse mussels (>50%), and not on Asian clams. Therefore their dietary selenium intake is likely to remain low. According to Beckon and Maurer (2008) only a relatively small proportion of clapper rail diet comprises Macoma clams (>7%), yellow shore crabs and snails account for less than 5% of the diet, and spiders and plant material account for 15% each. The preferred clapper rail diet, together with the fact that their principal habitats include low portions of coastal wetlands and tidal sloughs where the Asian clam is less common, are likely to limit the exposure of clapper rail to dietary selenium.

The recently published results of a study that investigated the reproductive success of clapper rail in six bay area marshes (including two marshes in the North Bay area: Corte Madera and Wildcat) during four breeding seasons from 1991 through 1999 (Schwarzbach *et al*. 2006) revealed that mean egg tissue selenium concentrations ranged between 1.89 and 2.22 µg/g-dw and were within the normal range for avian eggs (1 to 3 µg/g-dw: Skorupa and Ohlendorf 1991) signifying no effect on reproduction. Furthermore, the egg selenium concentrations declined significantly since the 1980s and were at half of the concentrations found in 1986-87 (mean: 4 µg/g-dw; range 1.6 – 7.4 µg/g-dw). As concentrations in eggs are the most direct way to determine avian embryonic exposure and effects we conclude that under current conditions the endangered clapper rail are not at risk from selenium exposure.

Surf scoter and Greater/Lesser scaup

Among the North Bay birds, only scoters and scaups are likely to be exposed to selenium concentrations in their diet that may exceed the screening levels, with the greater and lesser scaup and surf scoter being most at risk because of their feeding habits. These diving ducks are common in the North Bay and they feed primarily on benthic mollusks, especially clams and mussels, crustaceans and insects. The results from the 2002 bird study involving tissue and gut content analysis of surf scoters showed that the entire gut content of scoters caught in Suisun Bay was comprised of the invasive clam *C. amurensis,* while in scoters caught in San Pablo Bay the gut content consisted of 25% of *C. amurensis* and 75% of the soft shelled clam, Mya arenia (J. Hunt,SFEI, *pers. comm*). Average selenium tissue concentrations in scoters measured in Suisun Bay and San Pablo Bay were below 4 µg/g-ww indicating a 50% reduction compared to the levels observed in 1989 that exceeded 11 µg/g-ww (Figure 10).

The concentrations of selenium in greater scaups in 2002 and 2005 on average did not exceed 5 µg/g-ww; the levels in San Pablo Bay and Suisun Bay were slightly higher in the most recent samples than in 1986-1987. Nevertheless, the results show that typically, for both species, selenium concentrations in 2002-2005 were lower in most regions of the Estuary than in the peak concentration years of the late 1980s.

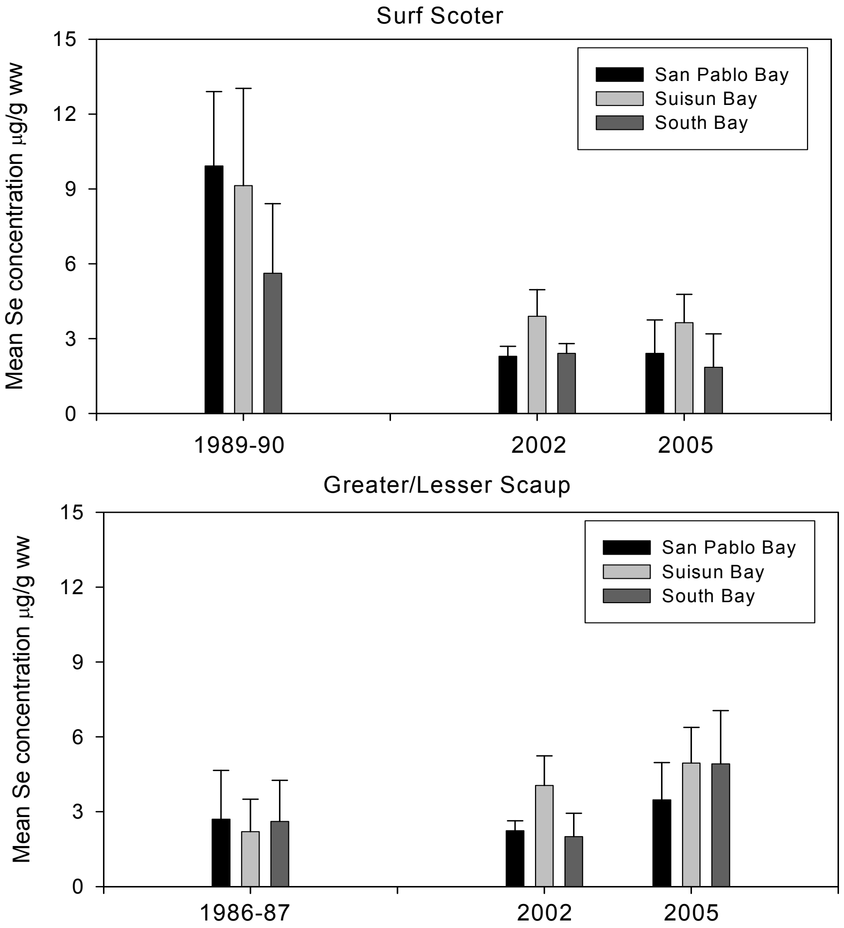

Figure 10: Selenium tissue concentration in diving ducks from San Francisco Bay

(columns represent average concentrations and bars show standard deviation)
Data: DFG 1987, 1988, 1991; SFEI- J. Hunt *pers. comm.*

A similar reduction in selenium concentrations in aquatic birds from Central Valley has been detected based on the data collected from 1986 to 2005 in the Grasslands area. Paveglio and Kilbride (2007) reported that selenium concentrations in the livers of mallards, pintails, coots and stilts from the North Grasslands declined by 38 to 68 percent throughout the 20-year period. For birds collected in North Grasslands in 2005 the average concentrations of selenium in livers varied from 5 to 8.5 µg/g-dw. The 95% confidence intervals (7.1 - 11 µg/g-dw) were highest in black-necked stilts. The authors affirmed that all 95% confidence intervals for the 2005 data from North Grasslands were below the potential reproductive impairment range of 20 to 30 µg/g-dw derived from the US FWS data.

The data from the National Irrigation Water Quality Program have shown that ducks exhibit greater sensitivity to embryonic selenium exposure than other species studied and the response functions developed for ducks represent a generic surrogate for other sensitive birds (Seiler *et al.* 2003). Yet predictions of the teratogenic effects based on the selenium-response functions showed that selenium concentrations of 15 µg/g-dw in eggs would have a minimal adverse impact (~EC01) and the duck eggs' exposure to 20 µg/g Se dw would cause incidence of teratogenesis to increase to 5 percent (EC05).

Moreover, studies indicate that both, selenium accumulation and depuration rates in birds, are rapid. It would take just over 70 days for waterfowl to return to background selenium levels once they leave the selenium rich source, and only within 8 to 10 days selenium concentrations are likely to fall below the known effect thresholds (Heinz *et al.* 1990, Wilson *et al.* 1997). The rapid depuration of selenium by diving ducks during their more than 50-day spring migration from San Francisco Bay to breeding grounds in Alaska and Northern Canada might be responsible for lack of detrimental physiological effects reported and for minimal amounts of selenium deposited in developing eggs. This way the potential for adverse effects in transient and migratory species that are most at risk from selenium in the North Bay is greatly reduced.

DeVink *et al*. (2008) simulated late spring migration exposure to environmentally relevant doses of dietary selenium in an experimental study with captive scaups. The authors found no treatment effect on body mass, breeding probability, or clutch initiation dates after a 30-day exposure to 15 µg/g and 7.5 µg/g of Se as selenomethionine, after which excess selenium was removed from the diets prior to laying. Moreover, the results showed that egg selenium concentrations decreased rapidly after selenium-supplemented diets were removed and within 12 and 8 days post treatment were below the teratogenicity threshold of 9 µg/g-dw. The overall conclusions indicated that these dietary exposures were not sufficient to adversely affect body mass or reproduction in scaup that subsequently migrated to uncontaminated breeding areas.

The selenium diets used in the study reflected the maximum reported concentrations (7.4 µg/g) in zebra mussels from sites along the St. Lawrence River and an environmentally elevated dose (15 µg/g) greater than the maximum reported concentration (11.5 µg/g) in zebra mussels from the Great Lakes. Areas surrounding Lake Erie have recently experienced significant increases in diving duck populations that are attributed to the invasion of the zebra mussel. Selenium concentrations in *C. amurensis* in the North Bay are very similar to those found in zebra mussels and used in the study. The levels in *C. amurensis* measured in 1999 ranged from 7.2 to 16.7 µg/g (mean 11.0 µg/g) and in 2008 the mean was 9.5 µg/g. One of the most compelling signs so far that the conditions in the Bay may have lesser than expected impact on diving ducks comes from the recent analysis of selenium in eggs of scoters. In 2005-2006 twenty three female scoters from the Bay area were marked with satellite transmitters and their migration was tracked to the breeding areas (Wainwright-De La Cruz, USGS, *pers. comm.*). Eleven fresh eggs were collected from three nests of the marked birds. The concentrations of selenium in these eggs were 1.71 +/- 0.12 µg/g-dw, well below those thought to be of concern for other sensitive bird species and within the normal range of concentrations:1 to 3 µg/g-dw; (Skorupa and Ohlendorf 1991).

Existing Screening Levels for Fish and Birds

Screening values reflective of safe selenium concentrations in water, sediment, food and tissue of aquatic organisms were reviewed and proposed in the past (Presser and Louma 2006, Hamilton 2002, Lemly 1998, Skorupa 1998). In establishing these threshold levels researchers considered numerous factors including the most sensitive endpoints, different life stages, type of exposure, dietary determinations and other conditions. To ensure protective conditions for all types of wildlife and habitats the suggested threshold levels tend to be set to the lowest value established from a limited number of experimental studies and field measurements, even though, a wide range of sensitivities to selenium might have been observed. This approach may lead to recommending screening values that are lower than background concentrations in areas naturally enriched in selenium. For example, minimum selenium concentrations in Yellowstone cutthroat trout in proximity to phosphate deposits in Idaho but not affected by the mine operations were reported to range from 0.1 to 4.7 µg/g-dw (Golder Associates 2006) while in other areas concentrations within the range of 1 to 2 µg/g-dw would be representative of background levels. In Central Valley, natural enrichment in selenium in soils contributes to elevated ambient selenium levels San Joaquin River.

Table 6 shows the screening level concentrations most commonly referred to in the scientific literature that encompass the variety of concerns. The concentrations exceeding the upper limits are likely to have adverse effects. The recommended ecological risk guidelines that were used to evaluate the success and effectiveness of the measures implemented to mitigate selenium contamination at the Grassland Bypass Project in Central Valley are shown in Table 7.

Table 6: Threshold selenium concentrations in fish and aquatic birds

Fish/Birds	Presser and Luoma (2006) [a]		Lemly (1998) [b]	
	Diet	**Tissue**	**Tissue**	**Measured Concentrations**
	µg/g – dry weight		µg/g – dry weight	
Fish Thresholds				
General	2 – 8	4 – 12	Whole body	6 – 9 no effect (<3) [c]
Sensitive Species	2 – 5	1.5 – 6		
Eggs	> 3	5 – 10	Eggs	6 – 17 teratogenic (<3)
Liver		12 – 15	Liver	4 – 7 no effect (<8)
Bird Thresholds				
General	3 – 7	3 – 10 (egg)	Muscle	7 – 19 no effect (<3)
Sensitive Species	2 – 5	6 – 7 (egg)		
	-	-	Eggs	4 – 9 no effect (<3)
Liver		20 – 30	Liver	23 – 32 teratogenic (<10)

a – Compiled from Presser and Luoma (2006) (Tables 13, 14 and 15)

b – Lemly (1998) (Table 1), values represent measured concentrations showing whether adverse effects are likely to occur

c – Values in parenthesis indicate concentrations typical for uncontaminated aquatic systems

Table 7: Ecological risk guidelines for selenium concentrations
(from Beckon *et al.*, 2001)

Medium	Effects on	No Effect	Concern	Toxicity
		µg/g – dry weight		
Warm water fish (whole-body)	Fish growth/condition/survival	<4	4–9	>9
Vegetation (as diet)	Bird reproduction	<3	3–7	>7
Invertebrates (as diet)	Bird reproduction	<3	3–7	>7
Sediment	Fish and bird reproduction	<2	2–4	>4
Avian egg	Egg hatchability	<6	6–10	>10
		µg/L		
Water (total recoverable Se)	Fish and bird reproduction (via foodchain)	<2	2–5	>5

Selenium Guidelines for Great Salt Lake (State of Utah)

In 2004 the State of Utah formed a Science Panel to develop a water quality standard for selenium in Great Salt Lake that would prevent impairment of aquatic wildlife. The Science Panel determined reproductive success in birds to be the most sensitive end point and used studies of mallards to recommend the guideline selenium levels in diet and eggs that would be protective of birds commonly nesting on the lake. In recognition of uncertainty the guidelines were initially expressed as a range and included diet selenium concentrations between 3.6 and 5.7 µg/g and egg concentrations between 6.4 and 16 µg/g (Utah DEQ 2008). Finally, Utah recommended the egg tissue-based standard of 12.5 µg/g-dw that is equivalent to 10% effect level concentration (EC10).

These numeric guidelines have been criticized for potentially allowing higher than acceptable levels of exposure in this unique ecosystem with very high environmental and commercial value (J. Skorupa, USFWS, *pers. comm.*). In addition, the availability of food sources rich in selenium and selenium ingestion rates might be extremely variable; hence, measuring selenium concentrations in dietary items may not provide the most sensitive indicator of birds' reproductive success. Subsequently, it was recommended that the concentration of selenium in the eggs be the preferred indicator that determines avian reproductive impairment.

Skorupa (2008, USFWS, *pers. comm.*) suggested that the State of Utah should aim at setting the water quality standard for Great Salt Lake to the value equivalent to no effect concentration (NEC) in avian eggs that could be inferred from the estimates of the EC10. The value of 7.7 µg/g for mallard egg hatchability determined with a generalized biphasic response model (Beckon *et al.* 2008) was considered to be the most technically valid approach for deriving the EC10. This resulted in recommendation of the NEC to be within the range extending from 3 to 7.7 µg/g with the lower boundary representing background means in avian eggs. A geometric mean of the boundary values was used to arrive at the best estimate of NEC for avian eggs that equals to 5 µg/g and this value is not being exceeded in the North Bay.

Given the uncertainties surrounding the magnitude of ecological risks the Science Panel recommended a tiered approach to implement the selenium standard of 12.5 µg/g-dw that requires an increased monitoring and triggers specific regulatory responses when selenium concentrations in eggs increase above 5 µg/g-dw.

Newport Bay Watershed Selenium TMDL

The most recent re-examination of black-neck stilt egg hatchability data by the USFWS staff for the purpose of establishing site-specific objectives for the Newport Bay Watershed TMDL (*report undergoing peer review*) generated two possible NEC for selenium in black-necked stilts: 5.8 µg Se/g dw and 10.2 µg Se/g dw. The value of 8 µg Se/g dw was then recommended as the egg tissue target to be sufficiently protective of the federally listed bird species that reside or forage in the Newport Bay watershed. The fish tissue target of 5 µg/g dw for both fresh and saltwater fish was deemed protective as a dietary target for piscivorous birds.

Site-Specific Thresholds Relevant to the North Bay

In summary, Table 8 shows site-specific concentration data and toxicological effects that are most relevant to the species and conditions in the North Bay.

Table 8: Summary of site specific data and toxicity levels evaluated for this project

Species in North Bay	Mean (standard deviation) [a]	Threshold Concentrations [a] - µg/g–dw		
Fish	µg/g-dw	LOAEL	Effect Threshold	Reproductive toxicity
White Sturgeon				
whole body		12.3 – 22.5	6.2 – 18.2	6 (9) [b] **8.1 (EC10)** [c]
muscle	9.2 (5.5)	12.1 – 36.8	4 – 29.0	
liver	24.1 (10.3)	10.4 – 37.4	3.9 – 28.7	
Sacramento splittail				
whole body		12.9	10.8	
muscle	2.4 (0.9)	15.1	12.3	
liver (Delta only)	11.5 (6.3)	26.8	24.8	
Birds	µg/g-dw	LOAEL	Effect Threshold	Reproductive success
Diving ducks		6.5 –27.3 (diet)	1.5 – 17.3(diet)	7.5 (diet-no effect) [d]
Surf scoter muscle	11.2 (4.4)			
Greater scaup muscle	13.0 (5.2)			
Scoter eggs	1.7 (0.1) [e]			5.0 (eggs-no effect) [f]
Bivalve tissue: local	2.5 (1.8) [g]	-	-	-
Bivalve tissue: invasive	1999: 11.0 (2.5) [h] 2008: 9.5 (2.6) [i]	-	-	-

a – Unless noted threshold concentrations based on the toxicity studies evaluated in Tetra Tech (2008b), Table 3-3 and Table 4-7 b – Toxicity thresholds estimated based on pooled data for coldwater fish (6 µg/g-dw) and warmwater fish (9 µg/g-dw) after Brix *et al.* 2000

c – Estimated by Beckon USFWS (*pers. comm.*, see Figure 8)

d – Diet representative of spring-staging with no adverse effects on reproduction (DeVink *et al.* 2008)

e – Concentrations in scoter eggs from San Francisco Bay found in wintering areas (Wainwright-De La Cruz, USGS, *pers. comm.*)

f – Egg tissue-based no effect concentration established for birds in Great Salt Lake (Utah DEQ 2008)

g – US Mussel Watch Program 1986-2005 (O'Connor and Lauenstein 2006)

h – USGS data for *C. amurensis* collected in 1999

i – Tetra Tech data for *C. amurensis* data collected in November 2008

4.3 Existing Water Column Objectives

To ensure protection of aquatic life, numeric water quality objectives for toxic pollutants such as selenium have been established by the USEPA and the California Toxics Rule (CTR).The aquatic life criteria include one-hour average (acute) and four-day average (chronic) concentrations of these pollutants to which aquatic life can be exposed without harmful effect. The criteria for selenium that currently apply are shown in Table 9. Although the USEPA approved the statewide selenium objectives for marine waters in California, they do not apply to San Francisco Bay. The USEPA found substantial scientific evidence that high selenium bioaccumulation was taking place in San Francisco Bay and, under these conditions, concluded that the saltwater criteria did not account for the food chain effects observed in San Francisco Bay. As a result the USEPA promulgated the freshwater National Toxic Rule (NTR) criteria for selenium in the San Francisco Bay/Delta. Water column concentrations in the North Bay do not exceed the NTR criteria.

Table 9: CTR water quality objectives for selenium

Water Quality Objectives	Chronic Objective µg/L (4-day average)	Acute Objective µg/L (1-hr average)
California (saltwater objectives)	71	290
San Francisco Bay and Delta (freshwater objectives)	**5**	**20**

4.4 Human Health Criteria

OEHHA (2006) developed equations to estimate fish contaminant goals (FCG) for selenium using a standard consumption rate of eight ounces per week (32 g/day). The FCGs are designed to estimate contaminant levels that pose no significant health risk to individuals consuming sport fish and could be used to establish fish tissue-based criteria for fish consumption advisories or pollution mitigation goals. They are similar in nature to the risk-based consumption limits recommended by USEPA (2000), however, the FCG calculations take into account contaminant nutritional requirements. Desired contaminant concentrations for a nutrient with a non-carcinogenic effect, such as selenium, is calculated as follows:

FCG = [(RfD x BW) – BDL]/CR where:

RfD – chemical specific reference dose (5×10^{-3} mg/kg-day)
BW – body weight of consumer in kg (70 kg default)
CR – consumption rate as a daily amount of fish consumed in kg/day (0.032 kg/day)
BDL – background dietary level in mg/day (0.114 mg/day)

The background dietary level was determined based on studies of nutritional requirements and the results of the National Health and Nutrition Examination Survey. The recommended dietary allowance (RDA) for selenium for general adult population is 55 µg/day and the mean selenium intake from diet only, surveyed among all individuals, is estimated at 113.7 µg/day. For those individuals who supplemented their dietary selenium the mean intake was found to be 116 µg/day. OEHHA recommends using the value of 114 µg/day as the background dietary consumption rate for computing FCGs for selenium. Using the above equation and assuming a consumption rate of 8 ounces per week of uncooked fish (32 g/day), which is also a rate used to begin issuing fish consumption advisories, the selenium FCG is 7.4 mg/kg. All known concentrations of selenium in fish in San Francisco Bay are well below 7 mg/kg–ww and therefore do not pose a risk to human consumers.

Similarly, the concentrations measured in the tissue of surf scoter and scaup ranging from 1.34 to 6.4 mg/kg–ww are below the guideline level.

4.5 Tissue-Based Numeric Target

Work is underway to revise the chronic aquatic life criterion for selenium on the national and state level (D. Fleck, USEPA Region 9 *pers. comm.*). However, because of the complex biochemistry of selenium in aquatic ecosystems and its bioaccumulative nature, dependent on resident species characteristics and site-specific conditions, it is unlikely that one criterion, when developed, would be relevant to the conditions in the North San Francisco Bay or other distinct water bodies.

As discussed in the sections above, we have reviewed the scientific literature and guidance documents to develop a numeric target that is applicable to the conditions in the North San Francisco Bay and protective of bird and fish species that are likely at risk from selenium exposure. Comparison of selenium bioaccumulation via waterborne versus dietary routes shows evidence that water-only toxicity tests could underestimate selenium risk and that selenium biotransformation by algae and zoobenthos adds substantially to the total exposure of higher trophic level organisms. Therefore, we are selecting the numeric target for this TMDL to be expressed as tissue-based concentration.

Even though both fish and birds have the capacity to regulate the levels of selenium in their bodies, the propensity of selenium to bioaccumulate and stay at higher levels is greater in fish than in birds. Despite strong bioaccumulation potential, diving ducks do not show significant adverse impacts. It has been demonstrated that waterfowl that use the area of San Francisco Bay as their wintering grounds depurate selenium quickly after leaving the area where food is enriched with selenium. Their tissue concentrations are likely to return to background levels before the birds reach their breeding grounds and their breeding success is not affected by selenium (Wainwright-De La Cruz, USGS, *pers. comm*., DeVink *et al.* 2008).

Our review of toxicological effects has demonstrated that selenium toxicity in the North Bay is only prominent in benthic-based food webs. Among the benthic-based food webs, the clam-eating bottom feeders such as white sturgeon and Sacramento splittail are most at risk, with white sturgeon being the most susceptible. Thus by establishing a numeric target that is protective of this fish we will ensure that all other species will also be protected.

While selenium toxicity has been studied predominantly in the freshwater environment and research has focused on warm water fish, new information is emerging showing the coldwater fish such as that in the North Bay are more resistant to adverse impact of selenium (Chapman 2007, Schlenk *et al.* 2003). It has been demonstrated that since sulfate levels should be higher in brackish and marine waters than in freshwaters, the numeric target established based on the freshwater toxicity studies is more stringent and, subsequently, offers an added level of conservatism to the target value.

The best available information indicates that the EC10 for white sturgeon should be no higher than 8.13 µg/g-dw (see Figure 8). This estimate takes into consideration gross developmental effects resulting from the transfer of selenium from fish through eggs to developing larvae when fish are most vulnerable. Most recently the USEPA indicated that the EC10 value of 8.1 µg/g-dw is being considered as the fish tissue criterion for San Francisco Bay. Nevertheless, scientific concerns remain whether this threshold offers sufficient protection for fish species like green sturgeon. At this time, due to uncertainties in scientific understanding and lack of guidelines for the desired level of protection for aquatic life in San Francisco Bay it is difficult to determine a single value as a TMDL target. Instead, we recommend a range of concentrations from **6.0 to 8.1** µg/g-dw as the proposed target. The lower range represents the upper end of the whole body selenium concentration range (4 to 6 µg/g) commonly associated with minimal effects in freshwater fish and is deemed protective of sensitive endpoints in the estuarine environment. The upper range corresponds to the EC10 established for white sturgeon, the fish identified in this TMDL as the species of concern in the North Bay. Overall, this range signifies the desirable level of protection for most sensitive fish species that reside and forage in the Bay. In developing the proposed values we considered various scientific arguments and all relevant data.

5 SOURCE ANALYSIS – SOURCES AND LOADS

Selenium mainly originates from natural sources such as sedimentary rocks, seleniferous soils, and selenium-rich mineral deposits occurring throughout California. Marine shale of Late Cretaceous period formed by sedimentary accumulation and mineralization of marine particulate matter are particularly rich in selenium (SWRCB 1989). Selenium from these sources could be concentrated and redistributed by geological and biological processes, and anthropogenic activities. Agricultural management practices leading to selenium enrichment in irrigation drainage water are often considered as the main cause of surface water contamination in California and the Bay Area. Irrigation remobilizes selenium by leaching it from the soils originating from marine sedimentary deposits. Weathering and erosion of selenium enriched sediments may contribute to the elevated selenium levels in nearby streams and groundwater. Fossil fuels such as coal and crude oil are naturally enriched with selenium. Thus, refining and cracking of crude oils, combustion of fossil fuels and solid waste, microbial activity, and industrial processes also release selenium to the atmosphere and surface waters.

There are several sources contributing selenium into the North San Francisco Bay. The main sources are industrial and municipal discharges including petroleum refineries, urban and non-urban runoff, erosion and sediment transport within the Bay, flow from Central Valley watersheds through the Delta, and atmospheric deposition. Brief descriptions of each source loading contribution, and the uncertainty associated with the load estimates are summarized in Table 10. The magnitude of selenium loads associated with these sources and their temporal variability are discussed in the subsequent sections[2]

During the wet season, riverine sources potentially contribute larger loads than known municipal and industrial facilities discharging to the Bay. While there is usually only limited inflow from the San Joaquin River into the estuary, selenium loads could increase significantly when water from the river reaches the Bay because of typically much higher selenium concentrations. However, it is the dry season that could be critical for selenium bioaccumulation due to its longer residence time in the Bay. Therefore, for source categories with seasonally changing load patterns and available flow information, both dry and wet season loads were calculated and compared.

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[2] Selenium load assessment presented in the following sections is based on the Source Characterization Report (2008a) prepared by Tetra Tech, Inc a technical consultant for the project.

Table 10: Characteristics of external and internal sources and loads of selenium in the North Bay

Source		Description	Dominant Se Forms and Species	Load [kg][a]
External	Municipal and industrial wastewater	POTWs and industrial wastewater effluents generally have low concentrations of selenium and they have not changed over the past 20 years. Total selenium concentrations in the effluent are measured and reported on regular basis.	**Predominantly dissolved Se**: selenate (60%), selenite (25%), organic and elemental Se (15%)	**230**
	Petroleum Refineries	Refineries contribute the largest load of selenium among point sources discharging to the Bay. The refinery effluent consists almost exclusively of dissolved forms of selenium with selenate, the less bioavailable form, being the dominant species since 1999.	**Predominantly dissolved Se**: selenate (56 - 64%) organic selenide (~20%) selenite (15 - 22%).	**540**
	Central Valley watersheds via Delta inflow	Delta inflow consists of flow from the San Joaquin and Sacramento Rivers, and forms the major source of selenium to the Bay. The rivers are also the main source of particulate selenium that provides a pathway to bioaccumulation of selenium in benthic organisms. Sacramento River dissolved Se concentrations are considered to represent regional background levels, they have been consistently low and have remained unchanged over the years. San Joaquin River carries seleniferous agricultural drainwater and has historically much higher concentrations of dissolved selenium. Much of San Joaquin River flows are currently diverted before entering the Bay.	**Dissolved selenium**: Sacramento River - selenate (50 – 70%) selenite (10 – 20%) organic selenide (10–20%) San Joaquin River - selenate (60 – 70%) selenite (3 – 10%) organic selenide (15–20%) **Particulate selenium**	**3940** (annual average) (1110 - >11000) **770** (part. Se annual average) (170 -1660)
	Urban and non-urban runoff	Urban and non-urban runoff from local tributaries – includes both agricultural and urban stormwater runoff, and may be a significant source of selenium during the wet season	Speciation not measured but assumed to be similar to Sacramento R.	**350-840** (>1500)
	Atmospheric deposition	Atmospheric deposition includes both dry and wet deposition to the Bay water surface, and is considered as a small selenium source	Wet deposition (selenite) Dry deposition	**20** (120) <**10** (130)
Internal	Erosion and sediment transport in the Bay	Can be either a source or a sink of selenium. Input from Bay sediments may include net sediment erosion, resuspension and diffusion. Dredging activities can also potentially contribute selenium to the Bay water column	**Particulate selenium**	**280**

[a] Unless noted, loads are expressed as total selenium. Values in bold represent the best estimate, values in parenthesis show the range and/or the highest estimate. Estimates are rounded to the nearest 10 kg

5.1 External Sources

Municipal and Industrial Wastewater Dischargers

Figure 11 shows locations of municipal and industrial facilities discharging treated effluent directly or indirectly to the North Bay. Among them, there are 22 Publicly Owned Treatment Works (POTWs), 6 minor industrial facilities and 5 petroleum refineries.

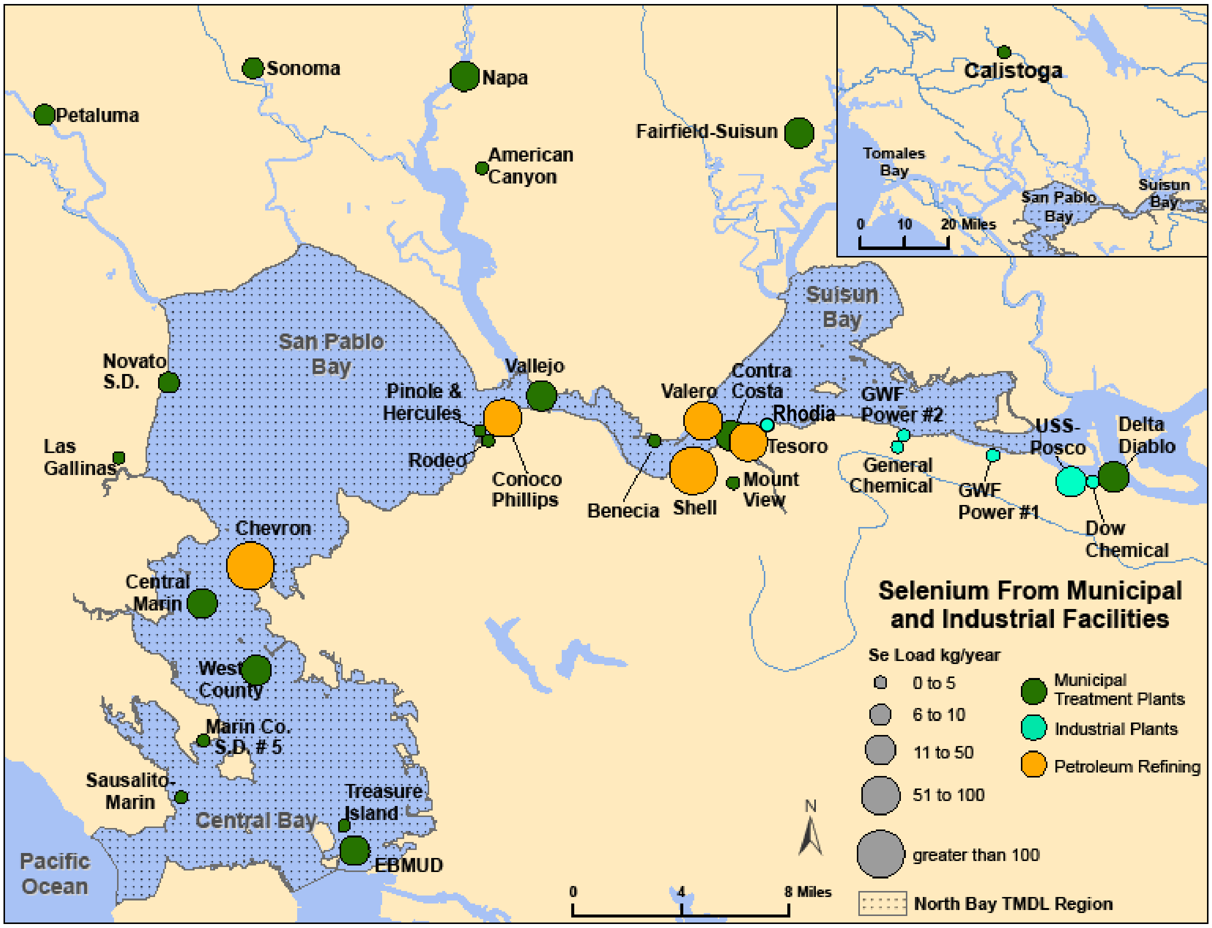


Figure 11: Point source dischargers in the North Bay

Publicly Owned Treatment Works (POTWs)

All most recent flow and effluent concentration data (1998 – 2007) reported by the POTWs as part of their permit requirements were used to evaluate the magnitude of selenium loads

(Table 11). Most municipal wastewater facilities treat effluent to the secondary level with the exception of City of American Canyon, Calistoga and Napa Sanitation District which have advanced level treatment. Discharge from these facilities generally follows a seasonal pattern of higher flows during wet season, most likely due to contribution from stormwater runoff.

Daily flow data and monthly selenium concentrations are usually available to compute loads. The average flow ranges from less than 1 million gallons per day (mgd) (City of Calistoga) to over 74 mgd (East Bay Municipal Utility District, EBMUD) with the maximum flow exceeding 150 mgd. Selenium concentrations in effluent are generally below 1 µg/L, with many samples below the detection limit (Table 11, Figure 12). Concentrations at two facilities with the largest discharges, EBMUD and Central Contra Costa Sanitation District (CCCSD), average 0.34 ± 0.19 µg/L and 0.34 ± 0.50 µg/L respectively. These most current concentrations are similar to the dissolved selenium concentrations observed by Cutter and San Diego-McGlone (1990) during 1987-1988 sampling of effluent at monthly intervals (EBMUD: 0.37 ± 0.10 µg/L, CCCSD: 0.53 ± 0.11 µg/L). This study also determined that the speciation of selenium in effluent from municipal wastewater was dominated by less bioavailable selenate (60%), followed by selenite (25%) and organic and elemental selenium (15%).

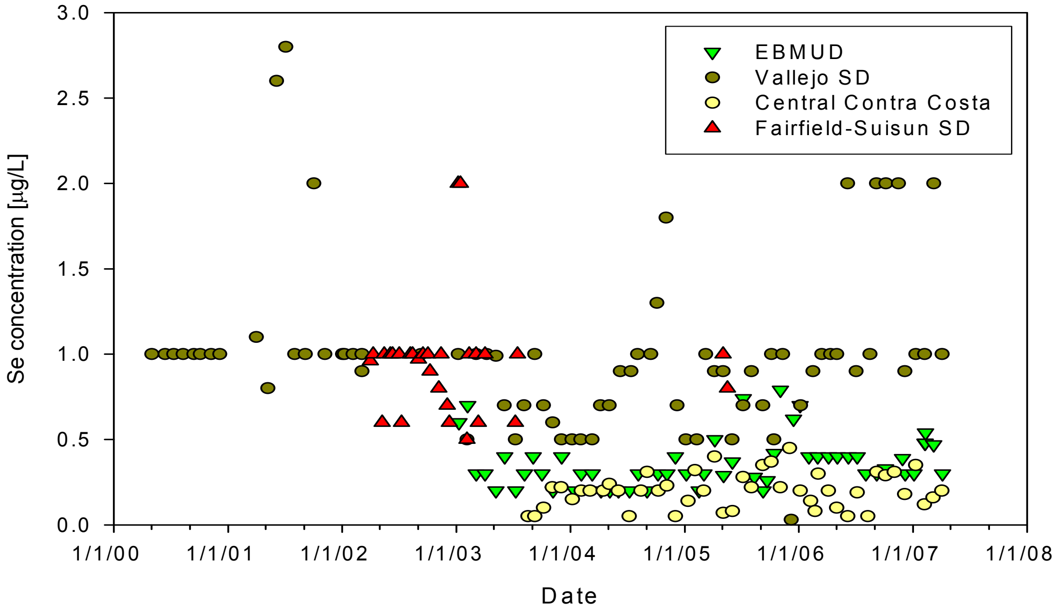


Figure 12: Selenium concentrations in effluent from selected largest POTWs

Two methods were used to estimate daily loads from POTWs. In the first method, the overall average daily maximum concentration for each facility was multiplied by overall average daily flow. In the second method, daily loads were first estimated based on daily flow and reported concentrations for all the available dates. Afterward, these estimates were used to compute an average daily load which was then extrapolated to an annual load. For concentrations reported below the detection limit, concentrations were assumed to be half of the detection limit. Sonoma Valley County Sanitation District reported selenium concentrations using a very high detection limit of 5 µg/L, therefore loads were not calculated for this facility.

Both computation methods resulted in similar load estimates (Table 11). POTWs on average discharge into the North Bay approximately 260 kg of selenium per year. The largest selenium load of 64.5 kg was calculated for Delta Diablo Sanitation District, where in early May 2004 for eight consecutive days, effluent selenium concentrations averaged above 28 µg/L. The duration and magnitude of high selenium concentrations suggested a problem within the wastewater facility or a spill incident. When these extreme concentrations are excluded from the assessment, the average selenium load from Delta Diablo SD is reduced to approximately 34 kg per year. Likewise, selenium load for Sonoma Valley Sanitation District could be extrapolated based on the performance of the City of Petaluma POTW that represents a comparable treatment technology, magnitude of discharge, and service area. The approximate load from this facility calculated with Method 1 and using the average selenium concentration of 0.65 µg/L is 3.7 kg per year. Taking into account the above adjustments (reduction of Delta Diablo SD and Sonoma Valley SD) the total average annual load generated by all POTWs is approximately 226 kg.

Table 11: Summary statistics of daily maximum effluent concentrations and estimated loads

Municipal dischargers	Time Period	No of samples	Effluent Concentrations µg/L				Average flow (mgd)	Estimated Loads kg/year [1]	
			Mean[2]	S.D.	Min	Max		Method 1	Method 2
City of American Canyon	2003-05	32	1.16	0.59	0.2	2	0.9	2.9	3.0
City of Benicia	1999-07	97	0.81	0.51	<0.3	5	3.0	3.5	3.4
City of Calistoga	2000-06	19	0.51	0.54	0.25	2.5	0.76	-	0.2
Central Contra Costa Sanitation District	1998-07	99	0.34	0.50	<0.05	4	45.8	21.8	15.0
Central Marin Sanitation Agency	1998-07	98	0.75	0.68	0.17	6.4	11.0	12.3	10.7
Delta Diablo Sanitation District [3]	1999-06	100	4.21	7.54	<1	37	11.5	64.5 (34)	64.1 (34)
East Bay Municipal Utility District	1998-07	294	0.34	0.19	<0.2	1.6	74.6	34.8	36.9
Fairfield-Suisun Sewer District	1998-03	95	0.75	0.38	0	2	17.0	19	18.5
Las Gallinas Valley SD Permit	2001-03	10	0.64	0.17	0.5	0.9	3.5	3.3	4.0
Marin Co. S.D. no 5	2000-07	47	1.93	1.4	0.5	6.0	1.0	2.7	1.9
Mount View Sanitary District	1999-06	37	0.62	0.60	<0.02	5	2.0	2.3	1.5
Napa Sanitation District (dry)	2002-04	13	0.57	0.21	<0.5	1	3.8	2	2.9
Napa Sanitation District (wet)	1999-04	26	0.27	0.25	0	<1	14	2.6	10.3
Novato Sanitation District (Ignacio dry)	1999-04	4	0.48	0.05	0.4	0.5	4.0	2.6	2.9
Novato Sanitation District (wet)		4	0.83	0.32	0.4	1	2.2	2.6	3.2
City of Petaluma	1999-07	60	0.65	0.23	0.35	1.4	7.6	6.9	8.3
City of Pinole and Hercules	2000-07	47	0.91	0.66	<0.1	4	3.2	4.0	4.2
Rodeo Sanitary District	2000-07	30	0.80	0.61	<0.1	3	0.8	0.9	0.9
Sausalito-Marin Sanitary District	1999-07	85	1.36	0.91	0.5	17.5	1.6	5.5	4.9
Sewerage Agency of South Marin	1999-04	133	1.39	2.01	0.15	12	3.3	6.4	5.1
Sonoma Valley County Sanitation District	1999-02	27	<5.00	0.00	<5	<5	4.1	3.7[4]	3.7[4]
US Navy Treasure Island	2000-04	46	0.29	0.17	<0.25	8.9	0.5	0.4	0.3
Vallejo Sanitation and Flood Control District	2000-07	79	0.84	0.52	<0.7	10.6	8.0	20.3	23.2
West County Agency /City of Richmond	2002-07	60	1.73	0.97	0.25	9	14.1	33.7	30.7
						Total		***258.7***	***260.2***

[1] Method 1: Loads computed based on overall average concentration and average daily flow; Method 2: Loads based on flow and concentrations for all available dates

[2] For values below detection limit, half of the detection limit was used in mean calculations

[3] Compliance monitoring data and the 13267 study data were used to estimate loads for this facility because of high variability in Se concentrations

[4] High detection limit of 5 µg/L, load in extrapolated based on average concentrations measured at City of Petaluma with Method 1

Industrial Wastewater Discharges

Loads from industrial facilities in the North Bay were calculated in a similar way to the second method used for POTWs. These loads are minor compared to other sources and average about 17 kg/yr (Table 12).

Table 12: Estimated selenium loads from industrial wastewater dischargers in the North Bay

Industrial Facilities	Daily load g/day	Annual load kg/yr
Dow Chemical	6.5	2.4
General Chemical	4.8	1.8
GWF (I)	1.1	0.4
GWF (V)	0.4	0.1
USS-Posco	31.0	11.3
Rhodia	2.8	1.0
Total	***46.6***	***17.0***

North Bay Petroleum Refineries

Petroleum refineries are the largest permitted source of selenium in the North Bay that tend to dominate selenium load during periods of low flow. The total refinery emissions estimated based on the 1998-2007 data exceed 530 kg/year. Mean selenium concentrations at the refineries vary from 11.9 µg/L (Tesoro) to 27.7 µg/L (Shell Martinez; Table 13) and show relatively large variations over time (Figure 13).

Table 13: Summary statistics of effluent concentrations at petroleum refineries

Refineries	Time Period	No of samples	Median	Mean	SD	Min	Max
Chevron	1999-05	308	11.2	12.1	5.9	2.3	48.0
ConocoPhillips (at Rodeo)	1999-07	448	14.0	15.5	8.5	1.0	49.0
Shell Martinez	1998-07	266	27.0	27.7	9.4	4.0	82.0
Tesoro	2000-07	367	11.0	11.9	5.1	1.0	41.0
Valero	1999-07	447	26.1	26.6	7.4	8.0	50.0

SD – standard deviation

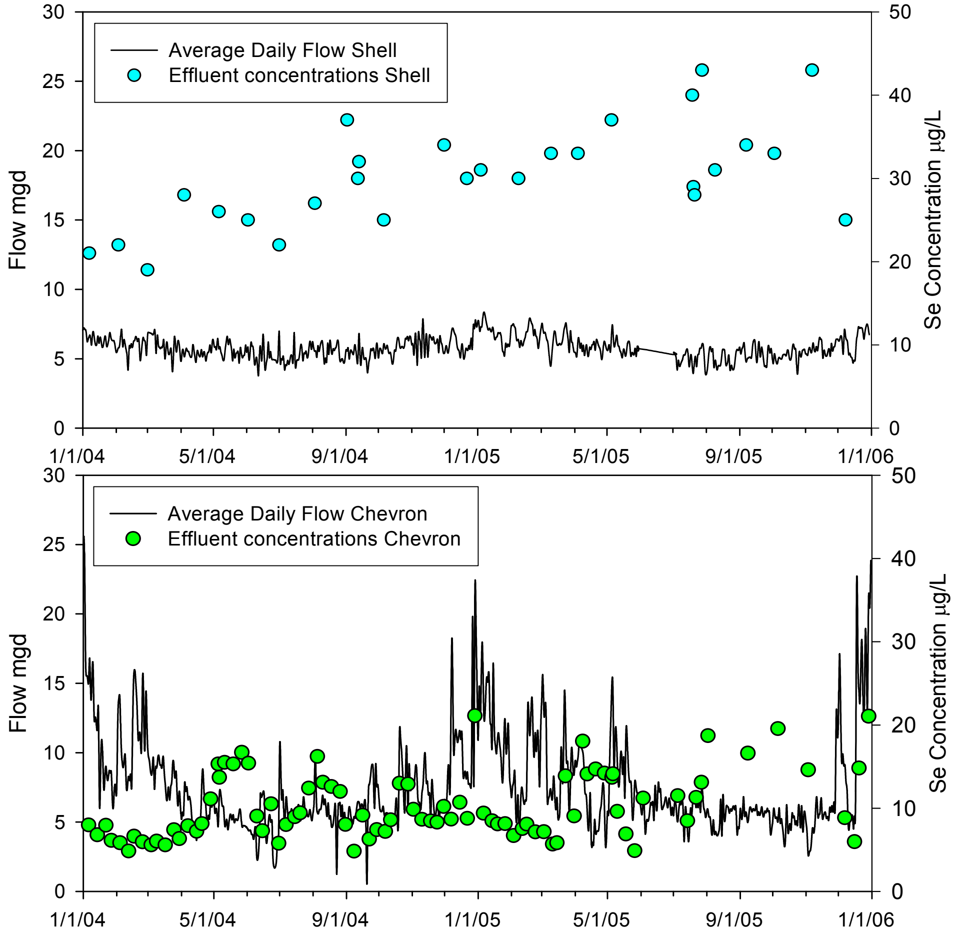


Figure 13: Effluent selenium concentrations and daily flow in Shell Martinez and Chevron refineries

Daily flow measurements at the refineries indicate some seasonal high flows, probably due to stormwater runoff. Similarly to municipal and other wastewater discharges, selenium concentrations in the effluents from refineries generally show no correlation with flow.

For the five petroleum refineries located in the North Bay, daily loads were estimated based on the continuous daily measurements of flow and the effluent daily maximum concentrations reported on a weekly basis. Mean daily maximum selenium concentrations for the refineries range between 12 and 28 µg/L. The estimated total daily load from these refineries is 1.47 kg/day or an average of 537 kg/yr during 1999-2007 (Table 14). Current loads are significantly lower than the previous years (1,407 – 3,382 kg/yr in 1986 – 1992) following the improvement in waste water treatment practices at the refineries (Presser and Luoma 2006).

Seasonal changes in loads from refineries were also evaluated by totaling the daily loads according to dry and wet season. The wet season was defined as October 1st to April 30th. The dry season was defined as May 1st to September 30th. Estimated annual selenium loads are relatively constant throughout the years (Figure 14). Average dry season loads are generally 62-78% of the average wet season loadings at four of the refineries. Average dry season loads at the Tesoro refinery are only 35% of the wet season loadings. Yearly loading does not appear to be affected by dry vs wet years.

The petroleum refinery effluents are dominated by selenate (56%) and organic selenide (30%), with selenite accounting for only 14% on average (compared to 64% of selenite in 1987-1988, Cutter and Cutter, 2004). Selenium speciation in refineries is similar to that found in municipal wastewater effluents.

Table 14: Estimated total selenium loads from petroleum refineries in the North Bay

Refinery	**Flow mgd**	**Mean daily load[1]**	**Mean daily load[2]**	**Annual load[1]**	**Annual load[2]**
		in kg/year			
Chevron	7.1	0.31	0.33	112.6	120.7
Conoco Philips	2.3	0.16	0.16	57.9	58.0
Shell Martinez	5.8	0.61	0.59	224.1	214.9
Tesoro	4.1	0.19	0.19	70.2	69.3
Valero	2.0	0.20	0.20	71.9	75.1
			Total	***537***	***538***

[1] Calculated as continuous daily flow multiplied by weekly concentrations and extrapolated to the rest of the week

[2] Calculated based on daily flow and concentrations on sampling dates only

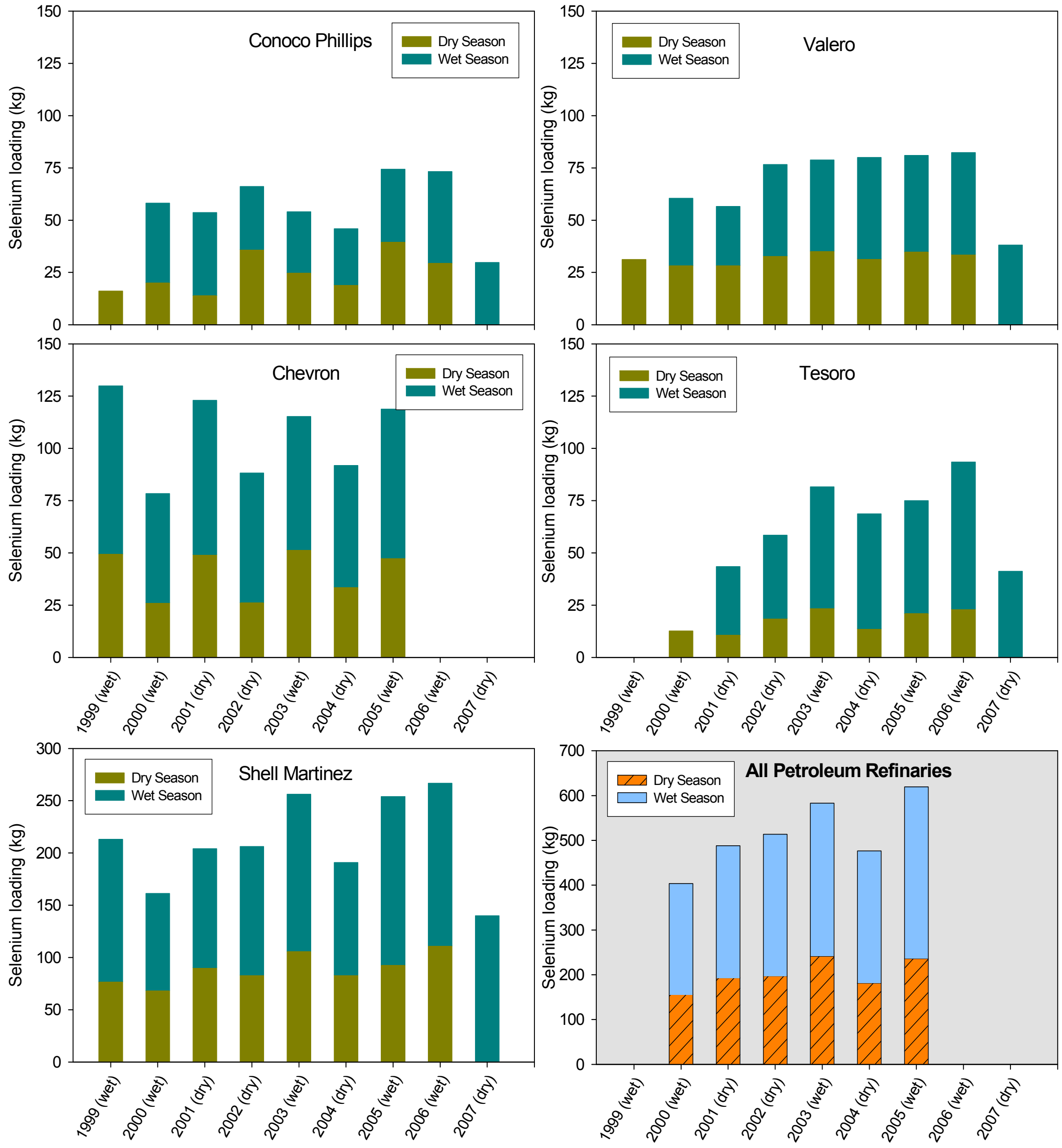


Figure 14: Dry and wet season selenium loads from refineries from 1999 through 2007

Urban and Non-Urban Stormwater Runoff from Local Tributaries

Local tributaries, that is, streams that discharge directly into the North Bay (Figure 15), can potentially contribute elevated selenium loads due to the presence of agricultural, urban and industrial land uses in their watersheds. Although these tributaries generate less than 4% of the total freshwater flow to the Bay, the relative proximity to the local sources of pollution, soil disturbances associated with urban development, and the dense stormwater conveyance system could amplify the delivery rate. McKee *et al*. (2003) have found that sediment export from small local tributaries averages approximately 100 t km^{-2}, which is much higher than the export from Central Valley (~14 t km^{-2}).

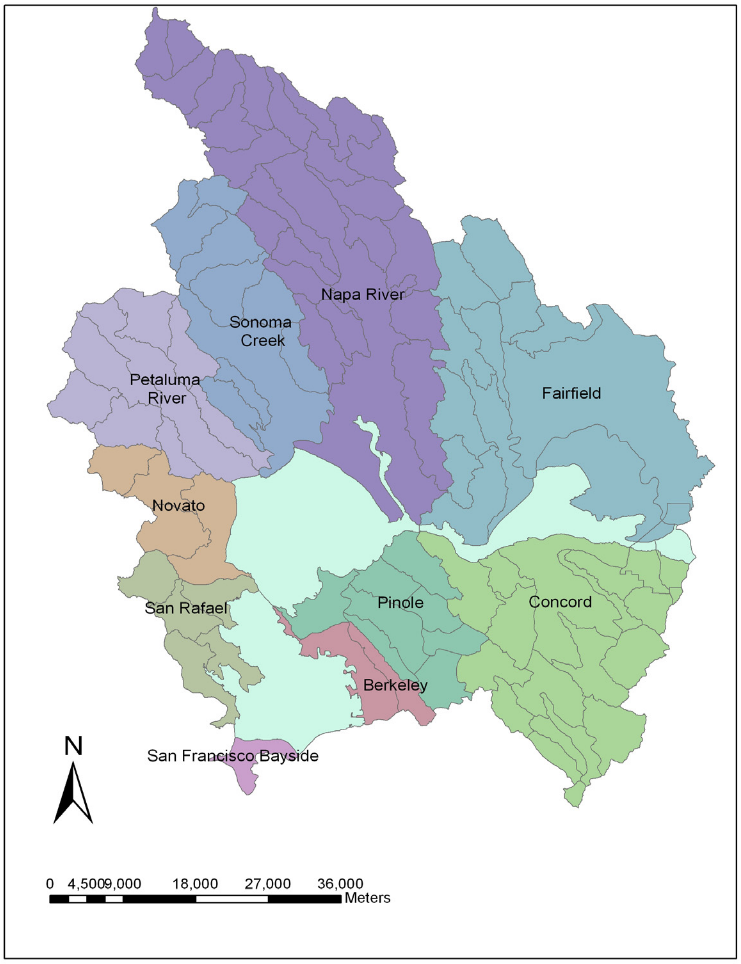


Figure 15: Hydrological areas surrounding the North Bay
(*Source: San Francisco Bay Institute*)

The available selenium concentration data for tributaries are limited and highly variable (Table 15). In 2001 – 2002 Surface Water Ambient Monitoring Program (SWAMP) monitored selenium in five tributaries in the North Bay and reported concentrations of 0.18–3.39 µg/L (median 0.94 µg/L) during the dry season, and 0.39–3.14 µg/L (median 0.90 µg/L) during the wet season (SFBRWQCB 2007a). Total selenium concentrations as high as 1.7 and 4 µg/L during wet and dry seasons of 2003-2004 were observed in Petaluma River (SFBRWQCB 2007b). Table 15 shows data available for the most downstream locations within the tributaries draining into the North Bay. These sites are considered to be indicative of the conditions within the entire watershed and therefore most suitable for the purpose of load estimates.

Table 15: Selenium concentrations at the SWAMP downstream monitoring locations collected during wet, spring and dry seasons

Water Body	**Site**	**Season**	**Year**	**Total Se** [µg/L]
Kirker Creek	KIR020	Wet	2003-2004	1.26
		Spring		1.30
		Dry		2.50
Mt Diablo Creek	MTD010	Wet	2003-2004	2.00
		Spring		0.40
Petaluma River	PET010 San Antonio Ck	Wet	2003-2004	1.30
		Spring		0.20
	PET310	Wet	2003-2004	1.70
		Spring		1.30
		Dry		4.00
San Pablo Creek	206SPA020	Spring	2001-2002	2.74
		Dry		1.60
Suisun Creek	207SUI020	Spring	2001-2002	0.90
		Dry		0.32
Wildcat Creek	206WIL020	Spring	2001-2002	0.39
		Dry		1.33
Average		***Wet***		***1.57***
		Spring		***1.03***
		Dry		***1.95***
		All Data		***1.45***

Bay Area Stormwater Management Agencies Association (BASMAA) collected selenium concentration data during a 1988-1995 monitoring study. The sampling sites in that assessment were mostly located in the Alameda County (16) with two sites located in the Contra Costa County. The monitoring program focused on measuring concentrations of pollutants in stormwater and was designed to determine pollutant loads in stormwater runoff dominated by different land uses (BASMAA 1996). Automated monitoring equipment was placed within the stormwater conveyance system to record runoff and to collect flow-weighted composite water samples. These monitoring stations received runoff from areas that were not larger than 1.5 square mile. Samples were also collected from selected waterways, including San Lorenzo, Alameda, Walnut and Dry Creek, to evaluate the quality of receiving waters during storm events. The waterway drainage areas varied in size from approximately 10 square miles (Dry Ck) to over 600 square miles (Alameda Ck).

Selenium concentrations reported by BASMAA are generally lower than values reported in subsequent SWAMP studies. Median concentrations were 0.40 µg/L during dry weather ($n = 7$) and 0.33 µg/L for storm event sampling ($n = 28$). By land use, median selenium concentrations were 0.29 µg/L, 0.35 µg/L and 0.30 µg/L for residential, open and industrial locations, respectively. However, the range of concentrations (0.06 – 0.90 µg/L) detected during the later period of data collection, which coincided with introduction of analytical methods with lower detection limit (< 0.05 µg/L), indicates that higher concentrations exceeding 0.1 µg/L were common. A wide range of selenium concentrations was detected in the monitored creeks that ranged from below detection limit to 9.9 µg/L. Concentrations exceeding 5 µg/L were recorded in all waterways during wet weather events.

Real time flow measurements and selenium concentrations in runoff from local tributaries are limited, thus the load assessments based on the available data are associated with large uncertainty. Therefore, to provide a better insight into the variability and magnitude of loads delivered into the North Bay, we used three methods to evaluate selenium tributary loads. The methods, data requirements and assumptions are summarized here.

Load Estimates Using Simple Model with SWAMP Data (Method 1)

This mass loading assessment employs a concept of a simple model to predict runoff volumes and the SWAMP data collected at the local tributaries. The volume of runoff is predicted using empirical runoff coefficients for discrete land use categories, rainfall, and the area of each land use. Pollutant loads are then calculated as the product of mean pollutant concentrations and runoff depths over specified period of time. The validity of the runoff model was tested and compared against the local data by Davis *et al*. (2000).
The contaminant load is calculated as follows:

$$Load = \sum_{j=1}^{n} (v_j * i * A_j) * C_{ave}$$

where $\boldsymbol{v}$ is runoff coefficient for land use j; $\boldsymbol{i}$ is the average rainfall for hydrologic unit and $\boldsymbol{A}$ represents the area of land use j in the hydrologic unit. $\boldsymbol{C_{ave}}$ is the average measured runoff contaminant concentration for the hydrologic unit.

Runoff volumes calculated by Davis *et al*. (2000) and concentrations measured in the SWAMP study were used to estimate loads from each watershed surrounding the North Bay (Table 16, Figure 15). Selenium was sampled during wet, spring, and dry seasons at four out of ten hydrological areas surrounding the North Bay. For those areas where site-specific data were not available, the average concentration from all the available monitoring locations was used to estimate loads. The average annual load of total selenium from local tributaries to the North Bay exceeds 900 kg/yr, with the Napa River and Concord watersheds identified as the largest sources. Higher total selenium loads from these watersheds are most likely due to larger watershed areas and high annual runoff.

Table 16: Annual runoff and selenium loads from local watersheds

Hydrologic Area	Total Annual Runoff (Mm^3/yr)[1]	SWAMP Stations	Mean Total Se Concentrations (µg/L)[2]	Total Se Load (kg/yr)
San Rafael	56		1.45	81.2
Berkeley	25		1.45	36.3
San Francisco-Bayside	8.8		1.45	12.8
Novato	47		1.45	68.2
Petaluma River	60	Petaluma River	1.7	102.0
Sonoma Creek	68		1.45	98.6
Napa River	180		1.45	261.0
Pinole	35	Wildcat, San Pablo	1.5	52.5
Fairfield	129	Suisun Creek	0.6	77.4
Concord[3]	106	Mt. Diablo Creek	1.2	127.2
Concord[4]	6.7	Kirker Creek	1.7	11.4
Total	***721.5***			***929***

[1] From Davis *et al*. (2000)

[2] Data collected by SWAMP (SFBWQCB 2007a, b); 1.45 µg/L is the mean concentration for all sites

[3] Concord hydrologic area: subunits 220731, 220732, 220733

[4] Concord hydrologic area: subunit 220734

These large watershed loads expressed on a per unit area basis do not differ significantly form other drainage areas. It is the most developed and highly urbanized watersheds of San Rafael, Berkeley and San Francisco Bayside that contribute on average well above 4 grams selenium per hectare (1.2 kg mi^{-2}), while Petaluma, Napa and Concord generating less than 3 grams per hectare (0.7 kg mi^{-2}).

Runoff in the Bay area is governed by the inter-annual variability in rainfall, which subsequently affects the magnitude of pollutant loads. The estimates of the 10th and 90th percentiles of rainfall could be indicative of load range for dry and wet years respectively. Davis *et al*. (2000) evaluated rainfall variability in the Bay area for the record period of 1961-1990. Taking into account these rainfall values and assuming average selenium runoff concentration of 1.45 µg/L (Table 15); the selenium load from local tributaries could vary from 686 kg in a dry year to 1750 kg in a wet year.

Load Estimates Using Available Measured Flow and SWAMP Data (Method 2)

The long-term average monthly flow measured by USGS and the seasonal selenium concentrations from the SWAMP study were used to estimate long-term average selenium loads at available gauging stations. Loads were calculated by multiplying flow and concentrations data for the same river. For tributaries without observed selenium concentrations, the overall average wet and/or dry concentration for all the North Bay sites was used (Table 15).

Long-term average monthly flow records at the USGS stations indicate that the majority of the flow is discharged during the wet season defined as October 1st through April 30th. Flow during the dry season (May 1st to September 30th) amounts to only a small fraction of the wet season flow (0.2 – 3.5%) with the exception of Walnut Creek and Pinole Creek for which the dry season flows could reach 13.1% and 5.8% of the wet flows, respectively. Similarly, the majority of the load is delivered to the Bay during wet season. Figure 16 shows a typical monthly pattern of selenium loads from representative tributaries in the North Bay. The highest annual load was estimated for the gauging station at Napa River near Napa (288.9 kg/yr) followed by Sonoma Creek at Aqua Caliente (97.1 kg/yr). Dry season loads are very small and average between 0.2 and 3.0% of the wet season loads for 6 of the 8 gauging locations (Table 17). A scaling factor based on the annual areal loading was used to extrapolate loads from the gauging location to the entire watershed area for each of the tributary. An areal loading from a nearby watershed was applied for the hydrological areas without data.

Estimated total selenium loads for the North Bay by hydrological area are summarized in Table 18. The total selenium loads calculated using the available USGS flow data and the SWAMP concentration data exceed 1510 kg/yr and are higher than the estimates based on modeled runoff described as Method 1. Once again, a large portion of the total tributary load was estimated to originate from Napa and Sonoma hydrological areas. Due to the lack of selenium concentrations for these two areas in the SWAMP dataset, an overall mean concentration of the whole North Bay tributaries was used to compute loads. Thus, these estimates are highly uncertain. Flow records for the Napa and Sonoma rivers also suggested higher runoff from these two areas compared to the rest of the North Bay (337 and 422 mm/yr for Napa and Sonoma, compared to ~200 mm/yr for the other tributaries). This will also contribute to the higher selenium loads than observed in other locations.

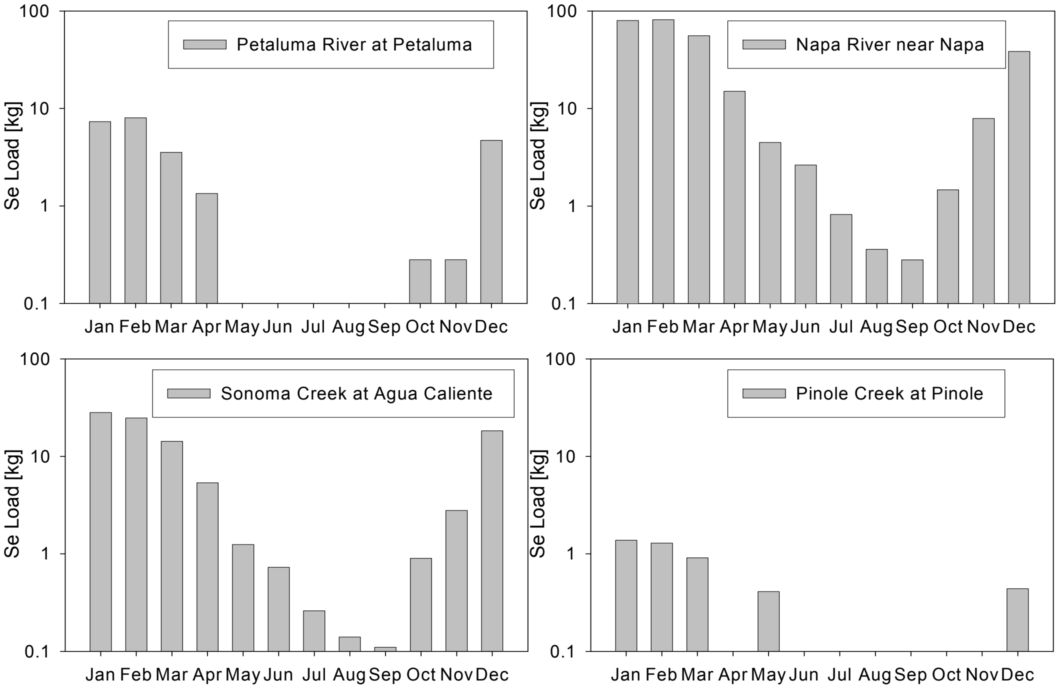


Figure 16: Average long-term monthly selenium loads at selected gauging locations

Table 17: Summary of selenium loads at the USGS gauging stations

	USGS Gauging Stations							
	11459500 Novato Ck at Novato	11459300 San Antonia Ck nr. Petaluma	11459000 Petaluma R. at Petaluma	11458500 Sonoma Ck at Agua Caliente	11458000 Napa R. nr. Napa	11181400 Wildcat Ck at Richmond	11183600 Walnut Ck at Concord	11182100 Pinole Ck at Pinole
Drainage area (mi^2)	17.6	28.9	30.9	58.4	218	8.7	85.2	10
Dry season load (kg)	0.5	< 0.1	<0.1	2.5	8.6	0.1	7.0	0.3
Wet season load (kg)	16.9	18.9	25.4	94.6	280.4	6.7	56.3	4.6
Dry as wet %	2.6	0.2	0.2	2.6	3.1	1.7	12.5	5.7
Total Load (kg/year)	17.4	19.0	25.5	97.1	289	6.8	63.3	4.9
Areal load (kg/mi^2)	*0.99*	*0.66*	*0.83*	*1.66*	*1.33*	*0.78*	*0.74*	*0.49*

Table 18: Estimated wet and dry season loads from local tributaries (*Method 2*)

Hydrological Areas	Area (mi^2)	Dry (kg)	Wet (kg)	Total Load (kg/yr)
San Rafael	60.9	1.6	58.8	60.3
Berkeley	33.8	0.4	26.0	26.4
San Francisco Bayside	11.1	0.3	10.7	11.0
Novato	71.03	1.8	68.6	70.4
Petaluma	145.8	0.3	120.2	120.5
Sonoma	165.9	7.1	268.6	275.9
Napa	362.1	14.3	465.7	480.0
Pinole	58.9	1.5	26.9	28.4
Fairfield	339.0	27.9	223.9	251.8
Concord	250.3	20.6	165.3	185.9
Total		***76***	***1435***	***1511***

Land Use-Specific Loads with Modeled Runoff and Concentration Data from BASMAA and SWAMP Studies (Method 3)

This assessment focused on evaluation of selenium loads generated by individual land uses in each hydrologic area. The method employs the simple model to estimate stormwater runoff associated with each land use within the drainage area and land use distribution (see Method 1, Davis *et al.* 2000). The model links contaminant emissions to rainfall and land use allowing for evaluation of potential differences in generated loads between years of different rainfall and types of land uses. It is assumed that mass loads are generated predominantly from diffuse sources and are representative of a long-term average runoff. As such, loads generated during dry weather conditions and resulting from, for example, bank erosion or groundwater inflows are not well represented in the assessment. Moreover, degradation or adsorption of pollutants while they are being transported downstream is not explicitly accounted for. However, this approach is widely accepted and tested against measured data with good results.

Loads are estimated for five broad land use categories (open space, agricultural, residential, industrial and commercial) based on estimated runoff from each land use type and land-use specific mean selenium concentrations. For the purpose of this assessment, urban land use includes industrial, commercial and residential areas. The “best estimates” of runoff coefficients and the mean selenium concentrations indicative of a particular land use are shown in Table 19. Land use specific concentrations were derived from BASMAA (1996) and

SWAMP studies (SFBRWQCB 2007a, b). Concentrations for agricultural land uses were assumed to be the same as open space. Due to the differences in concentrations reported by the two monitoring programs, values from the BASMAA project were used as the lower bound of concentrations from local tributaries, while SWAMP data were used as the upper bound.

Table 19: Land use specific runoff coefficients and mean selenium concentrations
(Tetra Tech 2008a)

	Land Use					**Source**
	Residential	Commercial	Industrial	Agricultural	Open Space	
Runoff coefficient (best estimate)	0.35	0.9	0.9	0.1	0.25	Davis *et al*. (2000)
Selenium concent. (low) µg/L	0.36	0.58	0.58	0.50	0.50	BASMAA (1996)
Selenium concent. (high) µg/L	1.55	1.55	1.55	0.85	0.85	SWAMP

The estimated loads range from 354 to 838 kg/yr depending on the mean concentration data used (Table 20). Open space and residential areas are among the major single contributors of selenium (301 and 250 kg/yr, respectively) mainly because they occupy a large proportion of every watershed. Many of the watersheds surrounding the North Bay experience very high level of urbanization. Urban areas that for the purpose of this assessment combine residential, industrial and commercial uses account for more than 50% in Pinole, San Rafael, Concord, Berkeley and San Francisco Bayside drainage areas. The estimated stormwater runoff from all urban areas is 316.8 Mm^3/yr that is approximately 44% of the total runoff. The loads from urban areas estimated based on the SWAMP concentration data exceed 490 kg/yr, or 59% of loads from all land use types. When BASMAA concentrations data are used the loads are reduced to 148 kg/yr, or about 43% of the total load from all land use areas. The land use specific loads for each hydrologic area are shown in Table 20.

Despite observed variability, Methods 1 and 3 provide similar results that are generally lower than that of Method 2 with the exception of the smallest and most urbanized drainage areas, such as Pinole or San Rafael (Figure 17). All three methods show similar load estimates for the highly urbanized drainage areas. This is not surprising as both methods (1 and 2) rely on the same approach to determine runoff volumes. Method 3 attempts to increase the estimate resolution by making the best use of the available concentration and land use data. All calculation methods show that one of the largest loads is generated by the Napa watershed for which the concentration data are not available. This may suggest that the load estimate is subject to greater uncertainties. Concurrently it could be seen that the highest selenium loads per unit area correlate positively with the level of development and the selenium generation rate for Napa watershed closely resembles other tributaries with similar land use composition (Figure 17).

Table 20: Selenium loads derived based on land use composition in local tributaries

Hydrological area	**Land Use Load (kg/yr)**					**Total Load (kg/yr)**
	Residential	Commercial	Industrial	Agricultural	Open Space	
San Rafael	42.4	17.4	2.2	0.0	13.6	*76*
Berkeley	14.4	10.4	11.7	0.0	0.9	*37*
San Francisco Bayside	4.8	8.3	0.4	0.0	0.0	*14*
Novato	19.2	15.1	2.2	1.7	18.4	*57*
Petaluma River	19.7	3.6	7.2	7.7	26.4	*65*
Sonoma Creek	13.7	4.4	4.4	9.7	36.3	*69*
Napa River	40.1	30.9	10.3	15.1	97.3	*194*
Pinole	15.9	6.2	14.9	0.0	9.3	*46*
Fairfield	18.8	20.3	16.1	11.5	67.0	*134*
Concord	60.7	30.5	24.6	1.1	31.6	*149*
UB[1] Load (kg/yr)	***250***	***147***	***94***	***47***	***301***	***838***
LB[2] Load (kg/yr)	***58***	***55***	***35***	***28***	***178***	***354***

UB[1] Load estimated using the upper bound mean selenium concentrations from the SWAMP data
LB[2] Load estimated using the lower bound mean selenium concentrations from the BASMAA data

The methods used to determine selenium loads from local tributaries into the North Bay take into account underlying data limitations, year-to-year and seasonal variability, and uncertainties in flow calculations. All these uncertainties are reflected in the estimated selenium load that according to the best available information could range from 354 to 838 kg/yr. We estimate that approximately half of this load originates from urban runoff.

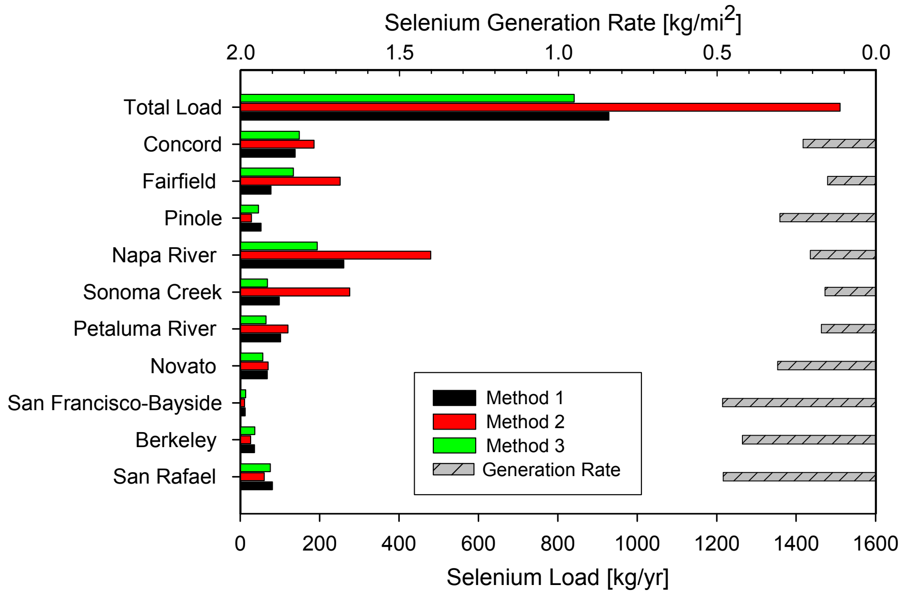


Figure 17: Comparison of load estimates from local tributaries using different calculation methods

(Se generation rates for each drainage area calculated using Method 3)

Direct Atmospheric Deposition

Atmospheric deposition of selenium occurs in dry and wet forms. Selenium is emitted to the atmosphere naturally as volatile dimethyl selenide, or as selenium dioxide and elemental selenium from fossil fuel combustion (Cutter and Church 1986). Deposition of selenium is part of a global cycle as gaseous selenium bound to particulate materials can be transported over long distances (USEPA 2002). Selenium in wet deposition consists of selenate, selenite, and elemental selenium. Rainwater samples from coastal California indicated that selenite is the major species in wet deposition for the region (Cutter 1978).

Dry and wet deposition of selenium has not been measured in the San Francisco Bay and estimates were made using data from other studies. However, similarly to other studies (USEPA 2002), it is likely that atmospheric deposition represents only a small load. Reported concentrations of selenium in precipitation are <0.1 - 0.4 µg/L in urban areas (Mosher and Duce 1989). Concentrations in precipitation measured in the Chesapeake Bay atmospheric deposition study are in the range of 0.07- 0.17 µg/L (USEPA 1996).

Given selenium concentrations of 0.07-0.4 µg/L ,an approximate annual rainfall of 450 mm/yr, and a water surface area of 648 km^2 in the North Bay (including Central Bay), direct wet deposition of selenium is in the range of 20.4 – 116.6 kg/yr. Wet deposition of selenium could be relatively bioavailable as selenite is the dominant form.

Dry deposition was calculated from air-phase concentrations of selenium. Reported concentrations in the air exhibit a large variation from 0.3 to 2.4 ng/m^3. Concentrations measured in the Chesapeake Bay range from 1.4 – 1.8 ng/m^3. Different deposition velocities were used to estimate dry deposition fluxes for the Great Lakes (0.1 cm/s, Sweet *et al*. 1998) and the Chesapeake Bay (0.26 cm/s low, 0.72 cm/s high; USEPA 1996). Selenium in the air is mostly associated with fine particles; therefore a lower deposition velocity is expected. Based on a concentration range of 0.3 – 2.4 ng/m^3 and deposition velocities of 0.1 cm/s and 0.26 cm/s, estimated dry deposition is in the range of 6.1 – 127.5 kg/yr. Considering the fact that the largest single source of airborne selenium is combustion of coal the atmospheric deposition of selenium in the Bay area is likely to be at the lower end of the estimated range.

Loads from San Joaquin and Sacramento Rivers Delivered via Delta

Selenium loads discharged from San Joaquin and Sacramento rivers remain highly variable despite water storage and extensive flow management taking place in the Delta watershed. Changing patterns of precipitation and runoff together with water diversions and complex interactions occurring at the Delta – Bay interface add to difficulties in estimating the loads. The relative flows from the rivers and other main components of the Delta water budget for an average flow year 2000 are depicted in Figure 18.

Despite San Joaquin River inflows to the Delta being an order of magnitude smaller than those of Sacramento River, San Joaquin River loads are consistently higher. This is because San Joaquin conveys selenium enriched agricultural drainage from Central Valley resulting in elevated selenium concentrations (0.68±0.02µg/L dissolved Se). Still, because of diversion and reverse flows in the Lower San Joaquin River, much of the agricultural drainage does not reach the lower estuary. Sacramento River selenium concentrations are much lower (0.07±0.02µg/L dissolved Se) and more typical of background concentrations in the region.

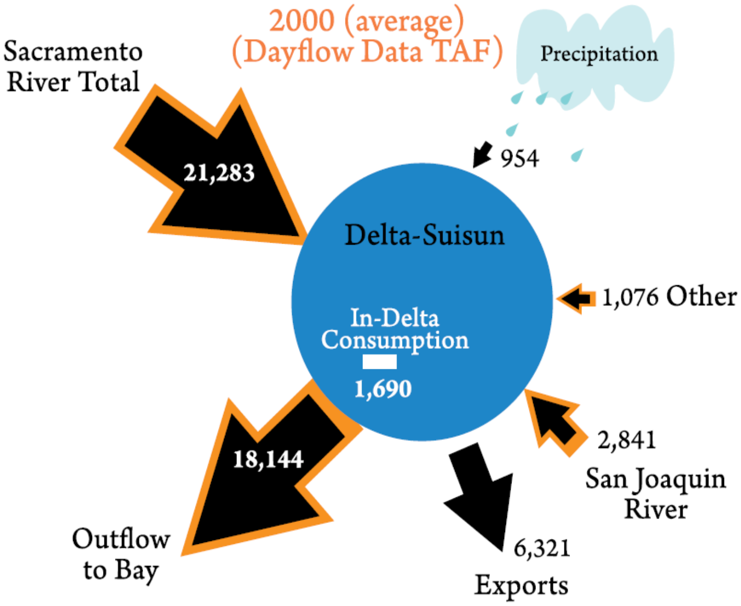


Figure 18: Water balance in the Delta for an average flow year 2000
Flow in thousand acre-feet (*From URS 2007*)

Three methods were used to estimate the relative contribution of the Sacramento and San Joaquin rivers to the Delta and to examine seasonal and annual load patterns from the Delta to the North Bay. The first method calculates selenium load discharged through the Delta using average dry and wet season concentrations measured at the two RMP stations (BG20 and BG30) above Mallard Island and the tidally corrected net Delta outflow generated by the Dayflow program. This approach was used in the past to estimate various pollutant loads from Central Valley to the Bay (for example see Davies *et al.* 2000).

The second method uses dissolved selenium concentrations measured by Cutter and Cutter (2004) in the Sacramento River at Freeport and data collected in the San Joaquin River at Vernalis to estimate individual loads contributed by both rivers. Then a “Delta removal constant” of 60% similar to the one described in Meseck (2002) is applied to the San Joaquin River load to account for complex interactions and likely selenium losses in the Delta. In the third method selenium loads from the Central Valley through the Delta are determined by estimating loads from the two rivers as described above and subtracting the load lost to the diversion of much of San Joaquin flow thru the aqueducts. This last approach is particularly effective for examining relative selenium load contributions of the two rivers to the North Bay.

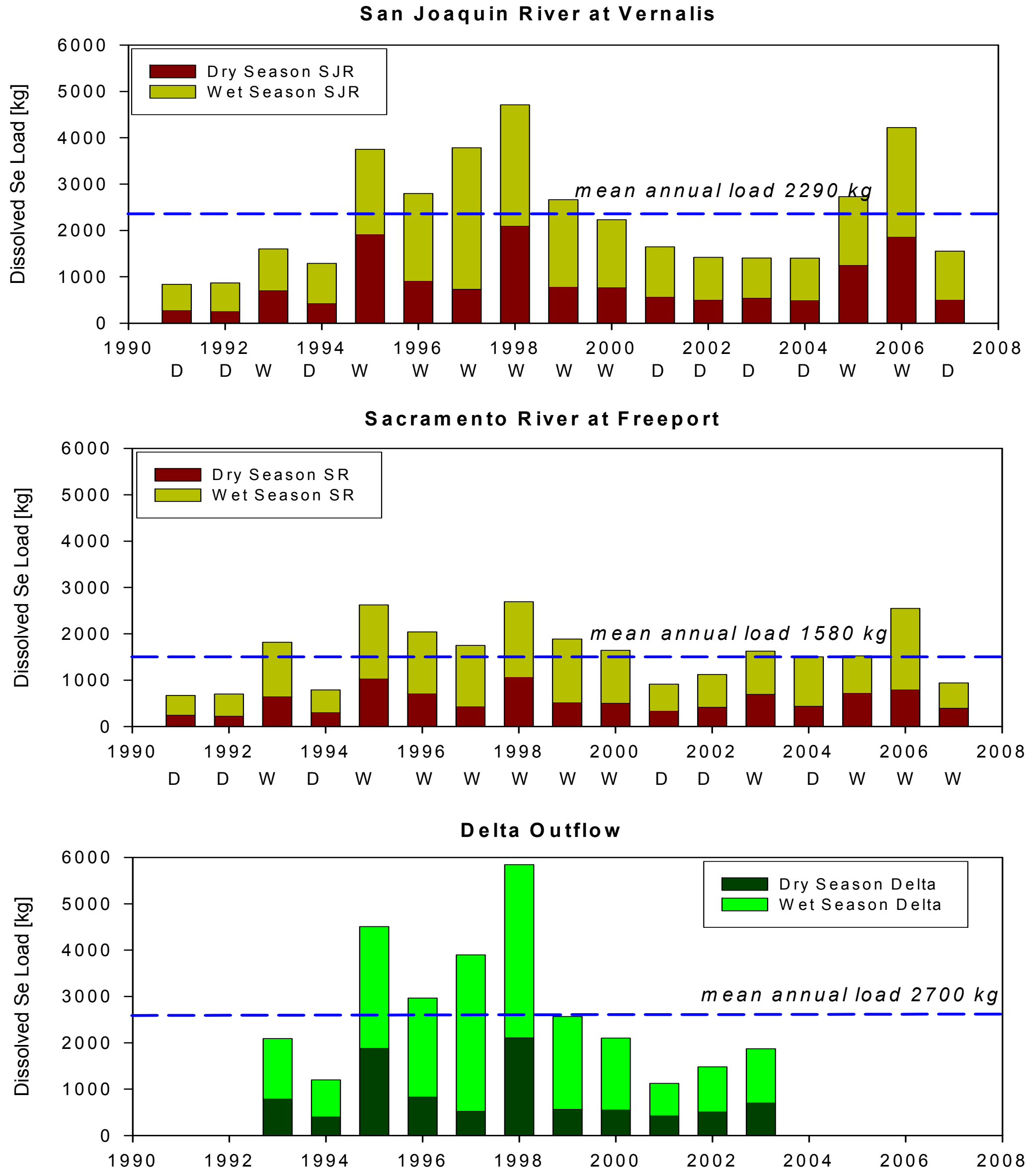
The explanation of the load calculation methods and the concentration data are described in detail in Tetra Tech (2008a).

Table 21 shows a summary of load estimates using different calculation methods and data sets and Figure 19 illustrates relative variability in the load delivered to the North Bay by season and year. Based on the dissolved selenium concentrations only, the estimated riverine loads range between 670 – 2690 kg/y for the Sacramento River at Freeport, and 840 – 4710 kg/y for the San Joaquin River in Vernalis. Dry season loads for both rivers on average do not exceed 40% of the annual load (Figure 19). The annual loads will also vary with water years. For example the San Joaquin River annual load may be higher than 4000 kg/y during wet years (e.g. 1998, 2006) and less than 900 kg/y in dry years (e.g. 1991, 1992). However, selenium loads that reach the North Bay through the Delta are likely to be more affected by flow diversions and water management than the overall hydrologic conditions.

Table 21: Dry and wet season loads to the North Bay from the Central Valley watershed

Source	Average Selenium Load [kg]			Assumptions and data used
	Dry	Wet	Annual	
Delta outflow	1007	2931	3938	Total Se load; RMP data, 1994-2006 (Method 1)
Delta outflow	910	1583	2493	Dissolved Se load, 60% removal constant for SJR (Method 2)
Sacramento River at Freeport San Joaquin River at Vernalis	564 863	1013 1426	1577 2289	Dissolved Se load, 1993-2003 concentration data (Cutter and Cutter, 2004)
Export through aqueducts Delta outflow	665 856	842 1840	1506 2596	Dissolved Se load, 1993-2003 concentration data (Cutter and Cutter, 2004) Method 3
Tributaries	76	1435	1511	Measured flow and SWAMP data

Estimates of dissolved selenium load originating from the Central Valley watershed using either the “Delta removal constant” or taking into account selenium export through the aqueducts are very similar and range between 2500 and 2600 kg/y. To account for particulate selenium load we employed the annual suspended sediment data at Mallard Island for water years 1995-2003 (McKee *et al.* 2006) and limited particulate concentration data from both rivers (Doblin *et al.* 2006). For the range of reported suspended sediment loads from 0.26 Mt/y (2001) to 2.6 Mt/y (1995) and the average particulate concentration (n=10) of 0.64 μg/g the estimated particulate load varies from approximately 170 to 1660 kg/y and the average annual load is 768 kg/y. The total average selenium load calculated as a sum of particulate and dissolved loads (estimated with Method 1 or 2) corresponds well to the first assessment method of total selenium load based on the RMP data and tidally corrected flow, which estimated the average annual load from the Central Valley watershed as 3938 kg/y (Table 21).



D - overall year classified as Dry; W – overall year classified as Wet

Figure 19: Estimates of dry and wet season riverine loads to the Delta and the Delta Outflow to North Bay

Considering the complexity of the Bay-Delta system, all three methods result in selenium loads that are fairly consistent. Method 1 with the different set of concentration data and flow independently ascertains that average dissolved and particulate loads are accurate and in general do not exceed 4000 kg/y. However, a large interannual variability could be expected depending on hydrologic conditions, magnitude of flow and water exports through the aqueducts.

5.2 Internal Sources

Erosion and Transformations of Selenium in Bottom Sediments

Conditions such as pH, oxidation-reduction potential, and the presence of metal oxides are among the key factors affecting the partitioning of selenium in the aquatic environment and controlling selenium transformations at the water column/sediment interface (USDHHS 2003b). In the North Bay bottom sediments, average selenium concentrations in samples from the depth of 5 to 15 cm range between 0.22 – 0.41 µg/g (G. Cutter, ODU, *pers. comm.*) and the mean sediment concentration based on RMP data is 0.25 µg/g. These levels of selenium are at the lower limit of the concentrations measured in 66 marine sediments from the northwest Pacific Ocean that ranged from 0.1 to 1.7 µg/g with a mean of 0.63 µg/g (Ihnat 1989). Recent RMP coring data show that unlike some other contaminants in the Bay sediments (e.g. Hg, Cu, PCBs) selenium concentrations stay relatively constant with depth and have remained unchanged for decades (Yee *et al.* 2010). Selenium in the bottom sediments is dominated by elemental selenium, which is considered insoluble, less mobile than other forms of selenium, and much less bioavailable. In a study by Doblin and others (2006) it was observed that Bay-Delta sediments averaged as high as 53-57% of elemental selenium. Selenium in bottom sediments can be mobilized to the water column through resuspension, erosion, diffusion and bioturbation. It can be also eroded and discharged through the Golden Gate to the ocean. Hence, the presence of elemental selenium in water column may indicate its origin from bottom sediments.

In previous Bay-wide TMDLs a top 15-cm layer of sediment was assumed to form an active layer that is in contact with biota or that can be resuspended into the water column. Sediment volumes are converted to sediment dry mass assuming that the Bay sediments are 50 percent solid by weight (range from 40 to 80%), and using densities of water and sediment of 1.03 kg/L and 2.65 kg/L respectively. The surface area of the North Bay extends for approximately 648 km^2. Using the mean sediment selenium concentration of 0.25 µg/kg, we estimate that a selenium mass in the active sediment layer is just over 18,000 kg with more than half of this mass being elemental selenium.

Localized sediment erosion also occurs due to decreases in sediment supply from the surrounding watersheds. Net sediment erosion was found to occur both in the Suisun Bay (~1.27 Mm^3/yr) and San Pablo Bay (~0.22 Mm^3/yr) (USGS 2001a, b). This rate of bed erosion will result in selenium load of approximately 277 kg/yr that can be potentially released to water column or exported into the ocean.

6 LINKAGE ANALYSIS – RELATIONSHIP BETWEEN SOURCES, TARGETS AND BENEFICIAL USES

Selenium impairment in the North Bay is related to elevated concentrations found in fish tissue. In order to evaluate assimilative capacity of the Bay and determine the most effective load reductions, it is critical to understand the important factors and sources causing selenium bioaccumulation in fish.

Selenium bioaccumulation is site-specific and driven by feeding habits of fish and differences in choice of prey. Particulate selenium and dietary uptake is the most important exposure pathway for aquatic organisms, especially predators, and that some types of food webs bioaccumulate selenium more efficiently than others. A conceptual representation emphasizing key factors affecting selenium transfer in two common food web types, benthic bivalve-based and pelagic crustacean-based in San Francisco Bay is shown in Figure 20.

In the North Bay adverse impacts of selenium bioaccumulation have been detected only in the benthic food web, and are particularly evident where the invasive clam *Corbula amurensis* dominates. A significantly slower rate loss exhibited by *C. amurensis* as compared to native clams and crustaceans, results in high tissue concentrations ranging from 4.3 to 14 µg Se/g dw (data collected in November 2008). This in turn poses a risk to the predators feeding on these clams, mainly white sturgeon and diving ducks.

6.1 Importance of Particulate Selenium in Managing Ecological Exposure

Although dissolved selenium dominates in the water column, the relatively small fraction (2-18.5%) that is particulate is far more available to bivalves and zooplankton, and is therefore of special significance to bioaccumulation observed in the North Bay. The direct intake of selenium by bivalves and higher level predators from the dissolved phase is extremely limited and, in fact, the pathway for nearly all selenium transfer to higher trophic levels is dietary exposure through particulate material (Luoma and Rainbow 2008). Estimates of invertebrate bioaccumulation with biodynamic modeling show that uptake of dissolved selenium is responsible for less than 2% of selenium found in tissue of bivalves (Presser *et al.* 2008). Only phytoplankton and bacteria are able to take up and concentrate aqueous selenium and this uptake varies widely across species.

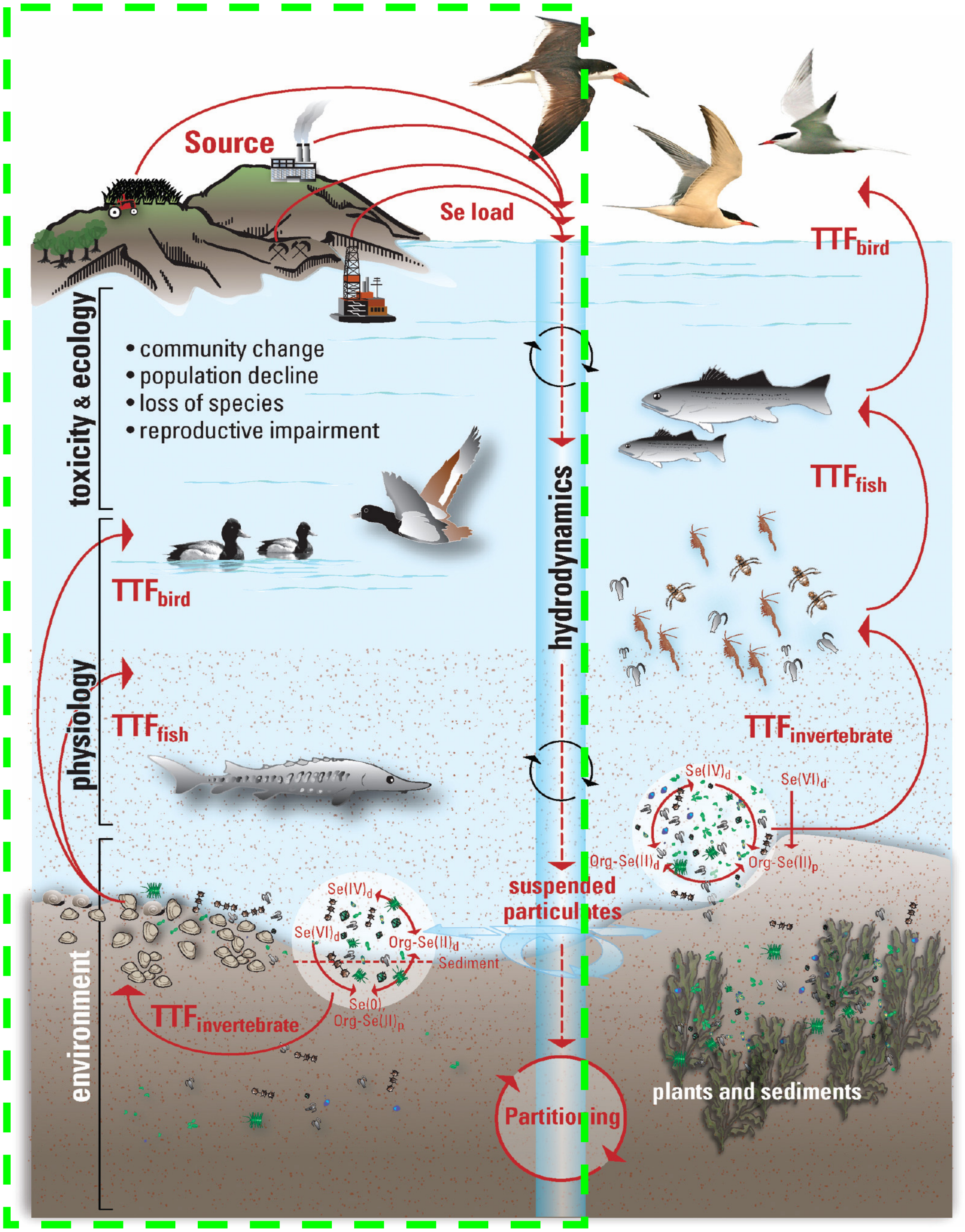


Figure 20: Conceptual model showing selenium biotransformations and implications for a benthic bivalve-based food web (*left panel*) and a water column food web (*right panel*)

(p - particulate, d-dissolved; from Luoma and Presser 2009)

Baines and Fisher (2001) demonstrated in laboratory experiments that marine algae cellular concentrations may exceed more than 100-fold ambient dissolved concentrations. These organisms will preferentially take up dissolved selenite and organo–selenide and rapidly convert it to organic selenides within their cells, thus becoming a rich source of particulate selenium to bivalves and other organisms that consume live and senescing algae. Uptake of selenate by algae is inhibited by sulfate content in water column (N. Fisher, Stony Brook University. *pers. comm*), hence, since the sulfate concentration in sea water is several orders of magnitude higher than that of selenate, under conditions in the North Bay uptake will be limited. Scientists now agree that the highest bioaccumulation takes place at the base of the food web (primary producers – algae, bacteria, fungi and plants) while the subsequent transfers to higher trophic levels, although biologically significant, tend to be much smaller (Chapman *et al.* 2009, Figure 21).

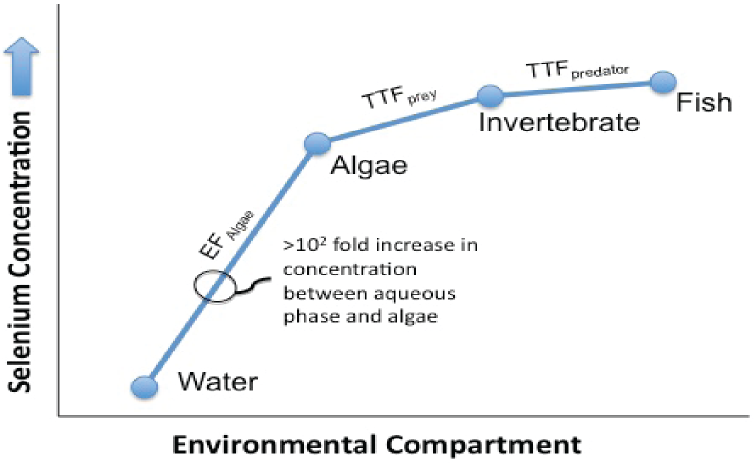


Figure 21: Selenium enrichment and trophic transfer in aquatic food web
(*Chapman et al. 2009 - SETAC Pellston Workshop*)

Particulate selenium in the estuary originates mainly from riverine input, with a smaller proportion of selenium coming from sediment resuspension, and in-situ transformations. Riverine inputs of particulate selenium can be a significant source of selenium to the North Bay as large amounts of sediments and living and non-living particulate organic material enter the Delta from Sacramento and San Joaquin watersheds. Particulate river load was estimated to range from 170 to 1660 kg per year (see Chapter 5 for discussion of selenium sources and loads). In riverine inputs, particulate selenium is mainly present as particulate elemental selenium, adsorbed selenite and selenate and particulate organic selenide.

6.2 Modeling Framework

We explored the available mathematical and empirical models to help identify conditions that could potentially exacerbate selenium associated risks and explain processes that affect relationships between environmental and anthropogenic loads of selenium in the North Bay and bioaccumulation in biota. Figure 22 shows a modeling framework comprising a numerical estuary model and a bioaccumulation DYMBAM model selected to simulate transformations and biological uptake processes in the North Bay (Tetra Tech 2008c, 2008d).

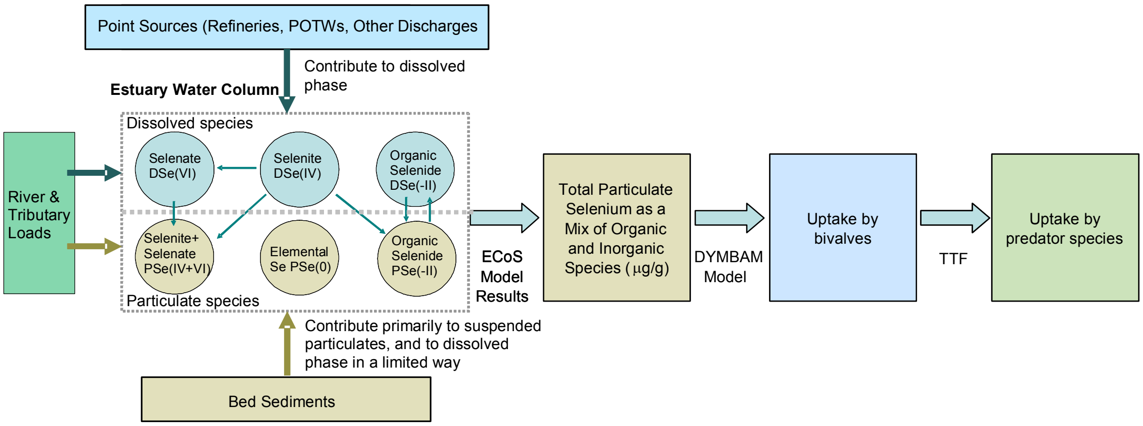


Figure 22: Schematic representation of the modeling framework linking selenium in water column and suspended particulates to bivalves, and then to predator species

The estuary model was developed using the ECoS3 framework and built upon the previous work of Meseck and Cutter (2006). The model was applied in a one-dimensional form with a daily time step. The estuary model simulates the biogeochemistry of selenium, including transformations among different species of dissolved and particulate selenium, salinity, total suspended matter (TSM), phytoplankton and water column concentrations, and the subsequent bioaccumulation of selenium in the North Bay. The aggregated output of the estuary model is subsequently used to evaluate selenium concentrations in bivalves and bioaccumulation of selenium through the food web by applying the empirical DYMBAM model (Presser and Luoma 2006) in a steady state mode.

The modeling framework, described only briefly in this report, provides a means to integrate and synthesize the existing information and offers a platform for evaluation of adaptive approaches to management of ecological exposure to selenium. The models were run to demonstrate how selenium discharges and other inputs can be related to the release mechanisms, secondary sources, and exposure pathways. For details on model application, assumptions, calibration and testing see Technical Memorandum 6: *Application of ECoS3 for Simulation of Selenium Fate and Transport in North San Francisco Bay* prepared by Tetra Tech (2010).

ECoS3 Estuary Model

The estuarine modeling framework ECoS3 was originally developed by the Center for Coastal and Marine Sciences at the Plymouth Marine Laboratory, UK, and subsequently used to simulate biological productivity, total suspended material, salinity, nutrients, and trace metal behavior in a range of European estuaries. As described in Harris and Gorley (1998), the ECoS3 framework contains modules that simulate transport and dynamics of different dissolved and particulate constituents in an estuary and can be applied in a 1-D or 2-D form.

It was first applied to model selenium in the North Bay by Meseck and Cutter (2006). In that application, equations to simulate transport and transformations of different species of selenium were formulated and the North Bay was modeled as a 1-D well-mixed estuary divided into 33 segments. The model domain starts from the freshwater end member at the Sacramento River at Rio Vista (X = 0 m; head) and extends to the mouth of the estuary at the Golden Gate (total length = 101,000 m). The head of the estuary is modeled as a closed boundary with seawater as an open boundary. The same spatial representation was also used in this project (Figure 23).

Salinity – Along the estuary gradient, salinity is governed by freshwater inflows, wind and tides, and simulated using advection and dispersion equations. During the high flow season, freshwater advection dominates and lower salinity is observed through the estuary. During low flow, salinity in the estuary increases as a result of reduced freshwater inflows. Water velocities are computed with cross section areas derived from the Uncles and Peterson model.

Sediment Transport – Potential sources of sediments to the Bay include the Delta input, local tributaries, in situ resuspension and erosion, and in situ production due to phytoplankton growth. In ECoS3, total suspended material (TSM) is represented as three different components: permanently suspended particles (PSP), bed exchangeable particles (BEPS) and phytoplankton (B).

PSP is defined as suspended material that does not sink and does not interact with the bottom sediments, and is modeled in a manner analogous to a dissolved solute (Harris and Gorley 1998; Meseck 2002). BEPS originates from sediment resuspension. A small portion of BEPS also originates from the riverine input. BEPS is modeled as a function of sediment resuspension and deposition, as well as advection and dispersion. The dispersion of BEPS is proportional to mixing that occurs due to both freshwater inflows and tides.

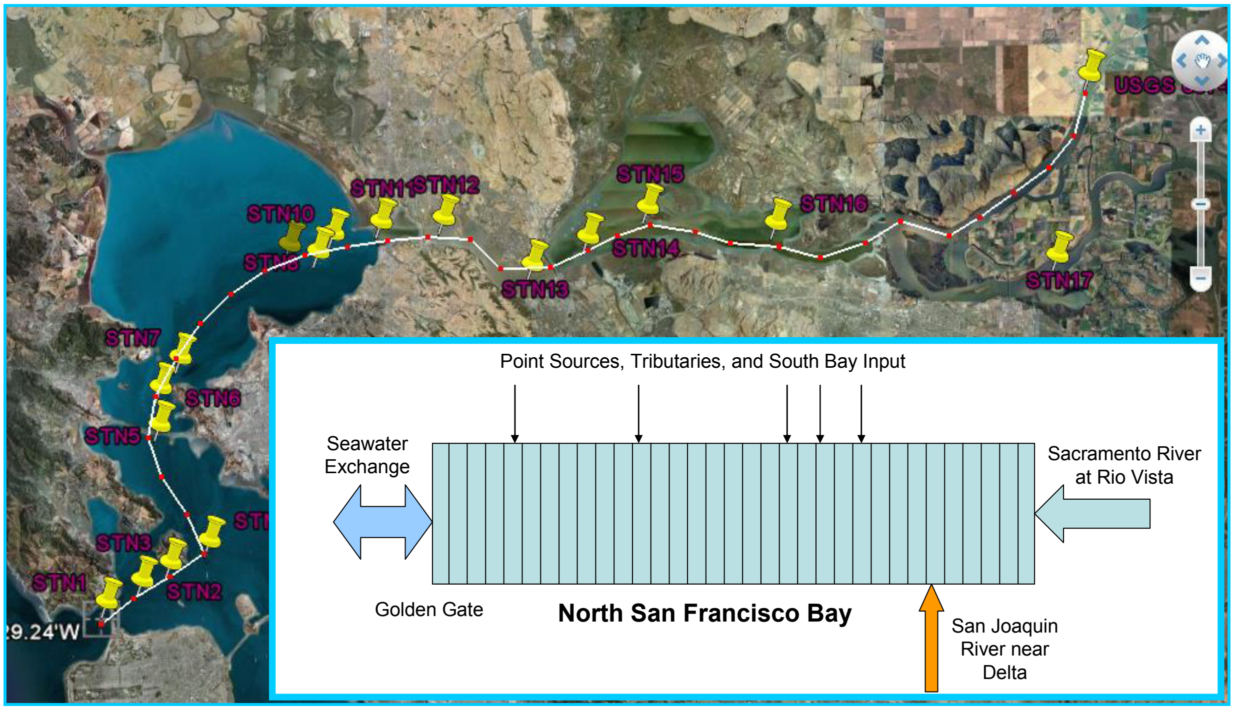


Figure 23: Spatial location of 33 model segments (*red dots*) **and schematic representation of the estuary showing boundary conditions and point source inputs**

Phytoplankton – The dynamics of phytoplankton play the key role in regulating selenium transformations. Dissolved selenium can be taken up by phytoplankton to form particulate organic selenium, which is bioavailable to higher trophic level organisms (Luoma *et al.* 1992). Phytoplankton is particularly affected by transport, growth and grazing by zooplankton and benthic organisms as well as settling and respiration (Meseck 2002) and modeled as a function of different sources and sinks. Benthic grazing can be a controlling factor in phytoplankton biomass as in laboratory experiments grazing rates observed for *C. amurensis* were found to exceed the specific growth rate of phytoplankton. Evident decreases in chlorophyll *a* concentrations observed in the Bay until recently, have been commonly linked to the invasion of *C. amurensis*. For further discussion of grazing effects and other limiting factors see Chapter 2 in Technical Memorandum 6 (Tetra Tech 2010).

Dissolved selenium – enters the North Bay from the Delta, local tributaries, refineries, municipal and industrial wastewater discharges, and diffusion from sediment. Speciation of selenium from these sources is generally dominated by selenate (Se^{6+}), followed by organic selenide (Se^{2-}) and selenite (Se^{4+}). In the water column, these different species of selenium can undergo biological and chemical transformations.

Transformations of dissolved selenite include oxidation to selenate, uptake by phytoplankton and adsorption and desorption from minerals. Transformations of dissolved organic selenide include oxidation to selenite and uptake by phytoplankton. Dissolved organic selenide is also generated through mineralization of particulate organic selenide. For selenate, the transformation includes uptake by phytoplankton and microbes. Oxidation of selenite to selenate was found to be a slow process which can take hundreds of years, while oxidation of organic selenide to selenite occurs over a timeframe of weeks (Cutter 1992). Similarly, phytoplankton uptake of dissolved selenite and organic selenide was found to occur relatively rapidly (Riedel *et al.* 1996; Baines *et al.* 2004). Transformations between species are simulated as first-order kinetic reactions. Uptake and transformation processes of dissolved selenium are shown schematically in Figure 24.

Particulate selenium – can originate from riverine input, sediment resuspension, and in-situ production (e.g., phytoplankton uptake of selenium). Different species of particulate selenium are assumed to be associated with PSP and BEPS. Phytoplankton selenium is assumed to be present only as organic selenide. Riverine inputs of particulate selenium are specified as selenium content on riverine loads of particulates (PSP, BEPS, and phytoplankton). Although phytoplankton can be measured as part of the TSM, for this project phytoplankton and phytoplankton-associated particulate organic selenium are modeled separately. Particulate organic selenium associated with PSP is assumed to be selenium associated with organic carbon other than living phytoplankton (e.g., detritus of phytoplankton, plant material, and bacteria).

In the model selenium content on riverine PSP is determined with calibrated parameters that are bounded by values reported in Doblin *et al*. (2006). Particulate selenium associated with BEPS is subjected to exchange with particulate selenium in bed sediments at the same rates as sediment resuspension and deposition. Seawater end member concentrations of particulate selenium are specified as constants (as selenium concentrations of PSP in seawater) for an open boundary. The transfer from dissolved selenium to particulate selenium includes mineral adsorption (mostly for selenite) and phytoplankton uptake of dissolved selenium for all three dissolved selenium species.

Selenium in sediments is modeled as a combination of initial concentrations modified by resuspension and deposition through sediment-water interaction, as well as some riverine input. Due to the balanced resuspension and deposition rates of sediment, the changes in selenium concentrations in bottom sediments are small.

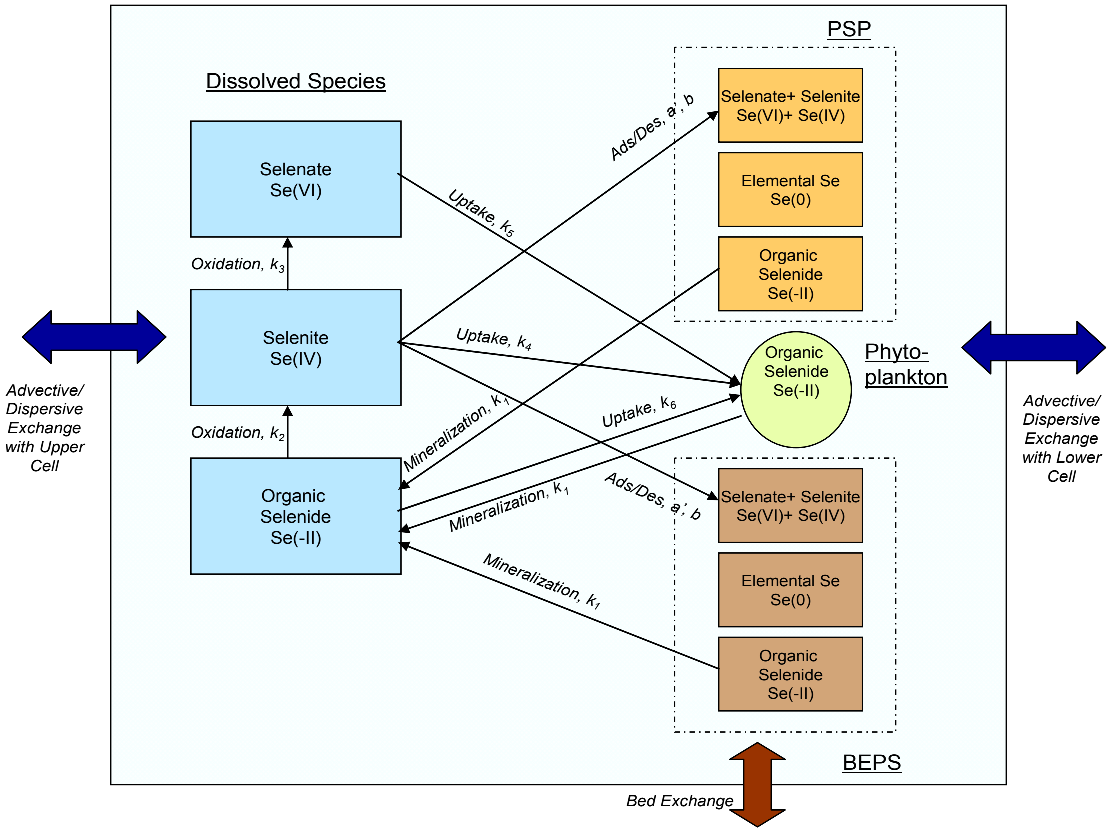


Figure 24: Interactions and transformations of dissolved and particulate selenium between different compartments in each cell of the ECoS3 model

DYMBAM Bioaccumulation Model

A dynamic multipathway bioaccumulation model (DYMBAM) describes contaminant accumulation and loss as a function of energy requirement in the lower trophic level organisms. DYMBAM uses species-specific empirically developed physiological rate parameters and environmental data representative of system conditions to assess and compare risks from metal exposure. In a steady-state application contaminant concentrations are expressed as a sum of waterborne and dietary uptake routes (Presser and Luoma 2006):

$$C_{ss} = \underbrace{\frac{k_u * C_w}{k_e}}_{\substack{\text{Water}\\ (\textit{dissolved})}} + \underbrace{\frac{AE * IR * C_p}{k_e}}_{\substack{\text{Food}\\ (\textit{particulate})}}$$

Where:

C_{ss} - steady state tissue Se concentration in clams
k_u - rate constant of Se uptake from water
C_w - Se concentration in water
AE - Se assimilation efficiency
IR - food ingestion rate
C_p- Se concentration in particulate material
k_e - the rate constant of loss

DYMBAM has been tested to be especially effective in determining selenium bioaccumulation in bivalves, copepods and polychaetes, and sufficient data exist to support assessments for benthic-based food webs with *C. amurensis* in San Francisco Bay. Applications of DYMBAM provide good compatibility with field observations despite simplifying assumptions and limited representation of bioenergetic responses in the model (Stewart *et al.* 2004). Model parameters to simulate selenium uptake by bivalves under a range of conditions are shown in Table 22. The ECoS3 model is used to determine concentrations of particulate selenium (organic selenide, selenite and selenate, and elemental Se) available on a daily basis. Then the species composition in the daily food intake by bivalves is assumed to be the same as simulated by the ECoS3 model, and used to compute average selenium concentrations in bivalve tissue according to the equation above.

Table 22: Parameters for DYMBAM model

	Assimilation Efficiency (%) for Particulate Selenium		
Ingestion Rates	elemental selenium	adsorbed selenite and selenate	organic selenide
0.45	0.2	0.45	0.8
0.25	0.2	0.45	0.8
0.45	0.2	0.45	0.54
0.85	0.2	0.45	0.80

Model Calibration and Evaluation

The basic physical functions of the model (salinity, total suspended material and phytoplankton) were calibrated using USGS data from 19 monitoring locations in the North Bay (http://sfbay.wr.usgs.gov/access/wqdata/). The main calibration time periods for these parameters are from January 1999 to December 1999. Water year 1999 was selected for calibration of the model because of the availability of detailed selenium speciation data sampled during both low and high flow periods. Water year 1999 also represents conditions for which detailed refinery discharge data are available. One-day time step was used in model runs, and the warm-up time was set to approximately 180 days starting from June 1, 1998.

The model calibration was done with a least squares minimization approach, using a fitting program provided by Dr. John Harris, the developer of the ECoS code. For every iteration, the sum of square deviation between observed and simulated values was calculated by the program and the parameters were adjusted for the next iteration to minimize the sum of square errors. After calibration the model was run to simulate the conditions in the Bay and the simulation results were validated for two hydrologicaly distinct years 1986 and 2001. Running a model for the year preceding the calibration time (hindcast mode) is considered to provide a good insight into the capability of the model to simulate conditions different from the calibration period in terms of hydrology and selenium loading. The results of these runs were compared with the observed data and the model performance was evaluated with two measures: correlation coefficient between predicted and observed values, and goodness of fit.

After initial evaluation of the model formulation and performance against the existing data, a series of model runs were conducted to gain more confidence in the model's ability to simulate selenium transformations across a range of conditions. The model was run under different input conditions and with different parameter values to assess the impact to selenium species concentrations. These tests offer better understanding of the functioning of the model by identifying processes and variables especially sensitive to the inputs, and point to the key variables where greater uncertainties may exist. The scope of the additional testing and the significance of each test are summarized in Table 23.

In general, the testing of the calibrated model demonstrated the ability of ECoS modeling framework to represent the key characteristics relevant to selenium fate and transport in the North Bay. The model performs particularly well in simulation of physical features of the Bay such as salinity. Although poorer match was achieved between the observed and simulated results for suspended sediments and phytoplankton, numerous runs clearly have shown that the model is able to adequately simulate selenium in various compartments. For all the parameters modeled, the model is able to represent average conditions better than spatial and temporal peaks in concentrations, and longer-term evaluations capture phytoplankton transformations reasonably well.

Table 23: Testing performed to assess model performance

Testing Performed	**Significance**
Sensitivity analyses	The calibrated model parameters are perturbed from their base case values to assess whether specific dependent variables respond significantly. Future model development and/or data collection must be targeted at the most sensitive parameters.
Changing Chlorophyll a	The model calibration and evaluation shows that chlorophyll *a* concentrations were sometimes poorly fitted with the ECoS framework. Additional model runs were conducted with varied chlorophyll *a* concentrations to better understand the importance of chlorophyll *a* to the predicted values of particulate selenium.
Changing uptake rates of dissolved selenium species	The uptake rates for selenate, selenite, and dissolved organic selenide are based on literature reports and calibrated to fit the data. Testing was performed to explore the impact of varying the rates over a wide range, from 10 to 100 times the rates in the base case calibration.
Different boundary conditions for riverine and seawater input	Particulate selenium concentrations in the riverine and seawater boundary have a significant impact on the concentrations in the Bay and the subsequent estimates of selenium levels in bivalves. Data to define these boundaries are scarce. Exploratory runs were performed over a wide range of values for both boundary conditions to evaluate simulated concentrations in the Bay.
Relative contribution of different sources of particulate selenium	Particulate selenium concentrations are the single most important constituent with respect to bivalve uptake, thus understanding of relative contributions from sources into the Bay: riverine, in-Bay sediment erosion or phytoplankton, and their effect on estuary concentrations is necessary for developing management options.
Spatial trends in particulate selenium	Spatial distribution of particulate selenium varies across the estuary. The model allows examining the main processes responsible for the small increases in particulate selenium observed towards higher salinities.
Mass balance	A mass balance of inputs and outputs provides a higher level check of the overall numerical representation. Selenium sources, outflows, and changes in stored mass in the water column are presented.

The fact that peaks in flow and flow-controlled attributes cannot be fully captured is commonly observed in many models used to simulate environmental conditions. The value of these models lies in their ability to link complex environmental processes and reproduce longer term trends. The ECoS-based modeling framework gives consideration to speciation effects and simulates temporal and spatial variations in selenium concentrations that compare well with the available field observations. It also offers a means to predict changes in selenium uptake by phytoplankton and bivalves and therefore to evaluate the effect of reduction strategies for the TMDL.

6.3 Effects of Load Change in the North Bay

Load Change Scenarios

The calibrated and validated ECoS3 model coupled with DYMBAM was used to evaluate the effects of hypothetical changes in point and non-point loads on the dissolved and particulate selenium concentrations in water column and bivalves to evaluate linkages to sources and to better understand the potential for system recovery. The selenium speciation and loads were varied and compared to the existing conditions. The effects of changing the most prominent selenium sources: San Joaquin River and petroleum refineries are shown in Figure 25 and discussed below.

The results show that the model is able to forecast even small changes in particulate selenium but other forms of selenium are less important in the North Bay system. Thus if selenium speciation in refinery effluent was hypothetically altered to include 10% of particulate selenium (see Figure 25, scenario 3), it would trigger the increase in selenium levels in biota. It was also confirmed that a potential for adverse impacts resulting from speciation change is especially prominent during low flow conditions. The hypothetical addition of 10% particulate selenium would also contribute to significant increases in selenium concentrations in bivalves during the dry season. Contrary to this scenario, even a 20% decrease in petroleum refineries' dissolved load, i.e. a hypothetical reduction by more than 110 kg Se per year (see Figure 25 scenario 4) based on the current selenium speciation that is all in dissolved form and dominated by selenate, will have no discernible effect on bivalve concentrations, nor will it contribute to a significant decrease in particulate selenium levels. This leads to a conclusion that reductions in dissolved selenium loads do not result in proportional change in particulate concentrations, hence the less significant than expected response observed in the Bay following petroleum refineries cleanup in 1999.

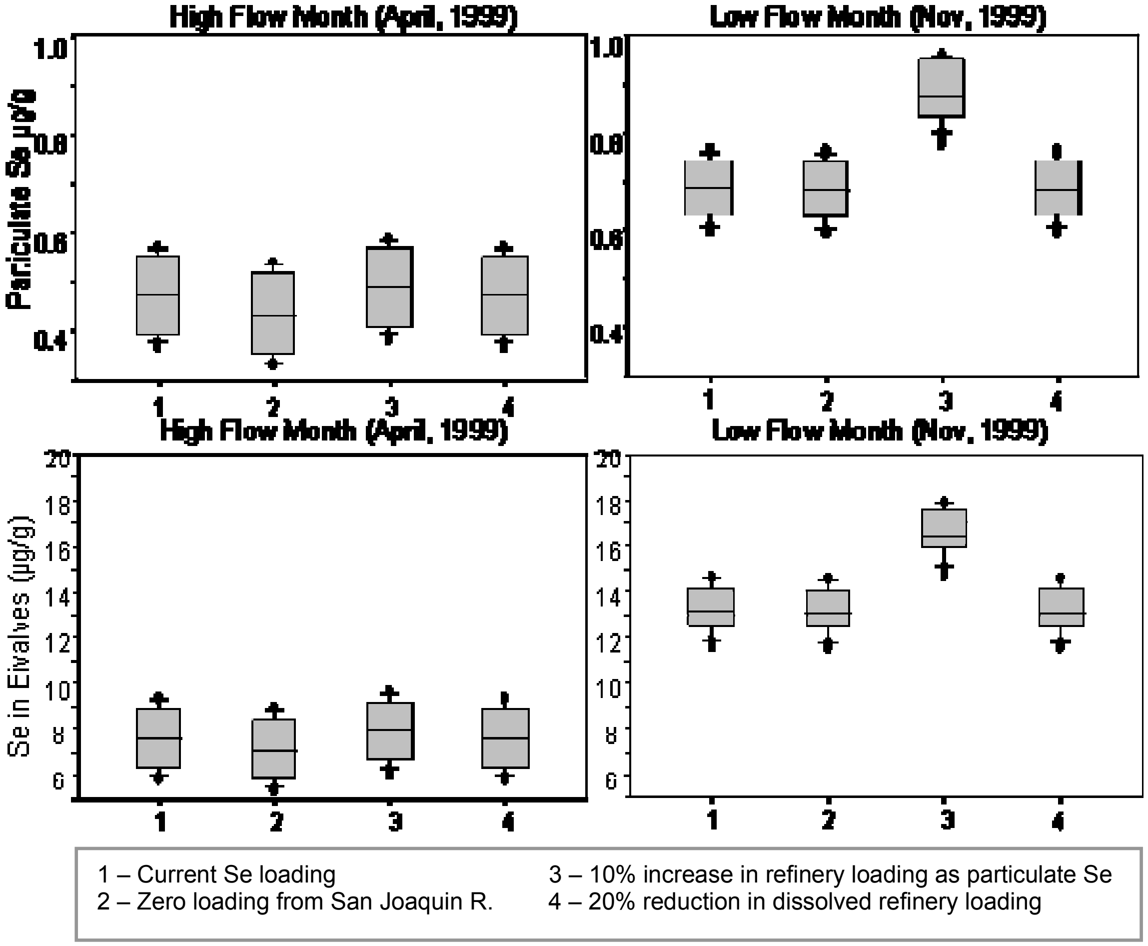


Figure 25: Predicted selenium concentrations for different loading scenarios

Complete elimination of the San Joaquin River dissolved load (e.g. see scenario 2) shows limited impact on dissolved and particulate concentrations. This is caused partly by the fact that most of the San Joaquin River inflow is diverted from entering the Bay and any changes in selenium loads are relatively small compared to the contribution of the Sacramento River load. However, if there is no continued reduction of San Joaquin River flow due to the State Water Project operations and other upstream diversions, significant increases in dissolved and particulate selenium concentrations in the North Bay may result.

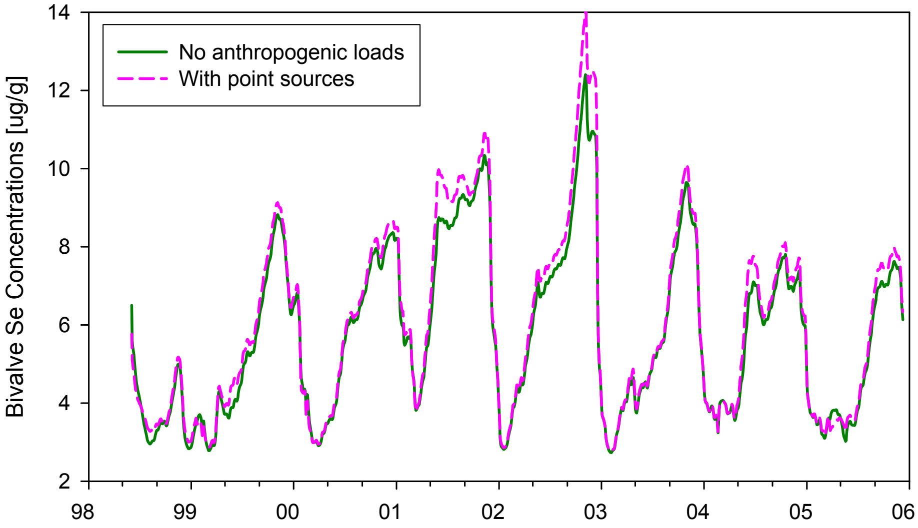
The overall sensitivity of the estuary to load changes from local tributaries and point sources is greater during dry months, especially during a dry year, i.e., for a given load change factor, greater change is observed during the dry periods, which relates to the overall lower inflow from Sacramento River and the longer residence times in the Bay.

Background Conditions

The natural baseline concentrations in the North Bay are defined by selenium inflow from Sacramento River mixing with selenium from the ocean. The inflow from Sacramento River at the background level selenium concentrations (~0.07 µg dissolved Se/L) carries on average 4.3 kg Se per day or 3.1 to 5.5 kg/day during dry and wet seasons, respectively. The maximum daily load during high flows may be as high as 7 kg/day, while the average refinery load is relatively small and stable throughout the year at 1.5 kg/day.

A scenario was run to evaluate the effect of background conditions on selenium levels in *C. amurensis*. This was defined as selenium loads that originate from natural background only without significant anthropogenic influences (e.g. refinery discharges, agricultural drainage, and POTW discharges), and assuming conservatively the Sacramento River concentrations as the natural background for the entire region (0.07 µg dissolved Se/L) including tributaries draining to the Bay and San Joaquin River, which is known to have higher background selenium concentrations (0.2 – 0.5 µg/L). On the other hand, in this scenario the impact of San Joaquin River discharge remains somewhat diminished because the model run reflects current (1999 – 2006) flow conditions with only a small proportion of San Joaquin River flow reaching the Bay. Discharges from petroleum refineries and POTWs were set to zero.

The results in Figure 26 show that under background load conditions the concentrations of selenium in *C. amurensis* may reach highs similar to those currently seen in the North Bay indicating that this invasive species plays a key role in amplifying available dietary selenium in the benthic food web. Much lower selenium concentrations are found in native clams due to low ingestion rates and higher loss rates. The results also indicate that for very short periods of time in low flow conditions (October – November) anthropogenic loads may be at levels that potentially can impact concentrations in bivalves. However, there is no evidence to suggest that this is really occurring. High selenium concentrations found in bivalves at the end of low flow/dry period may also reflect the growth cycle of *C. amurensis*. For example, in San Pablo Bay, they usually reproduce in spring and depend on phytoplankton blooms for food during spawning and growth, reaching their highest size in fall. Thus, selenium concentrations found in the bivalve tissue may also result from the overall longer accumulation period (see section 6.4 for further discussion).



Ingestion rates (IR) = 0.45, AE = 0.2, 0.45, 0.8 for elemental, inorganic, and organic particulate Se

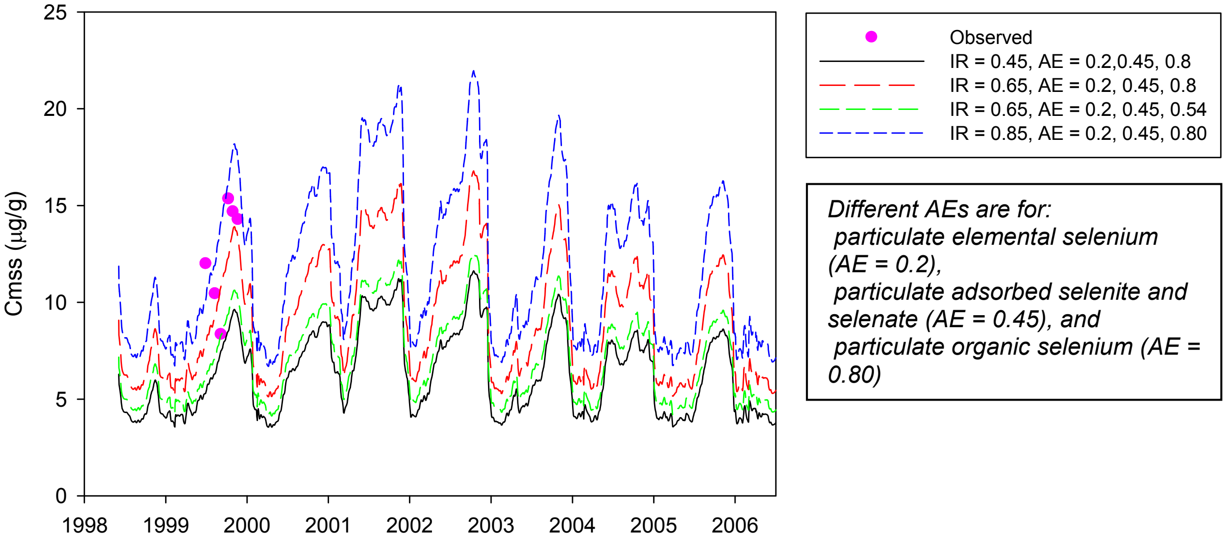
Figure 26: Model predicted selenium concentrations in bivalves under background load conditions and with point source loads

Although a simulation with all point sources of selenium removed is essential to our understanding of selenium bioaccumulation potential, these predictions are associated with large uncertainties. For the calibration of the model we relied on the best available data and scientific judgment in defining boundary conditions at the freshwater end member in Sacramento River.

Due to the lack of measured particulate data in the freshwater reach, the available data from the nearest suitable location (Rio Vista) were selected that allowed for the best fit with the measured concentrations in the Bay. The salinity of these samples was at zero or near zero signifying that at the time of the measurement the freshwater flow was prevalent. While this is a valid approach, the Rio Vista area is known to be tidal, hence some uncertainty still remains as to whether the origin of particulate material was in fact the Sacramento River or the Bay. Validation of baseline particulate conditions in the Sacramento River is vital and cannot be resolved without collecting new data.

6.4 Predicted Concentrations in Bivalves and Sturgeon

Figure 27 shows predicted selenium concentrations in bivalves for an array of ingestion rates and assimilation efficiencies. The results are calculated using the DYMBAM model with the assumption that the composition of particulate selenium species in the daily input of food ingested by clams is the same as simulated by the ECoS3 model. The observed peaks in concentrations are influenced mainly by seawater/freshwater mixing and chlorophyll levels, which change from year to year. The clam feeding rates (biodynamic model parameters) are based on studies with *C. amurensis* in the laboratory, and represent the high end of the experimental values (Lee *et al.* 2006).



Different AEs are for: particulate elemental selenium (AE = 0.2), particulate adsorbed selenite and selenate (AE = 0.45), and particulate organic selenium (AE = 0.80)

Figure 27: Simulated selenium concentrations (Cmss) in bivalve *C. amurensis* near the Carquinez Strait compared to observed values at the USGS station 8.1

For 1999 – 2006 the predicted ranges in bivalve selenium concentrations are between 3 and 22 µg/g and compare well with the measured concentrations (Stewart et al. 2004). After reaching the apparent peak in 2001-2003 the forecasted bivalve concentrations show a considerable decline, which has been also confirmed by the recent measured data showing concentrations below 10 µg/g from 2004 through 2006 (USGS 2010, Figure 28).

However, the levels of selenium in these clams are likely to fluctuate and stay elevated compared to other benthic organisms. Not only do these clams exhibit a high propensity to bioacumulate selenium based on their bioenergetic characteristics but they also appear not to differentiate between food sources of selenium, like other bivalves. For example, in laboratory experiments the Asiatic clam *C. fluminea*, more efficiently assimilates selenium associated with algae (66–87%) than selenium associated with oxic sediments (20–37%), but no consistent difference was found between assimilation efficiencies from organic and sedimentary food types (19–60%) for *C. amurensis* (Lee *et al*, 2006). In addition, it appears that other factors such as rainfall and Delta flows that control salinity particularly in the North

Bay, may alter conditions in which *C. amurensis* could thrive from year to year and thus affect selenium levels.

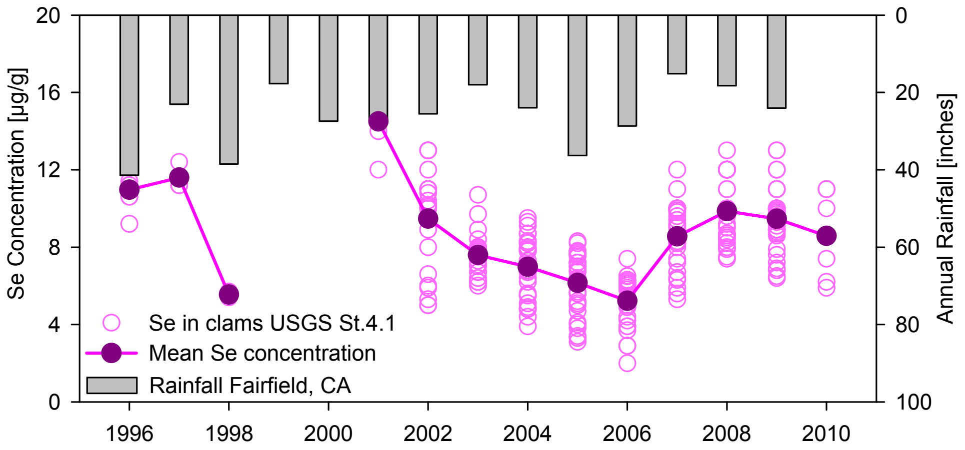


Figure 28: Concentration of selenium in *C. amurensis* measured at USGS station 4.1 and annual rainfall

The DYMBAM approach could also be used to forecast selenium bioaccumulation in fish except that kinetic uptake parameters for sturgeon are not known. Instead, transfer of selenium from food (e.g. bivalves) to fish can be represented by relationships between concentrations in fish tissue and concentration in dietary items (Luoma and Presser 2009). This ratio is called the Trophic Transfer Factor (TTF) and combines three biodynamic constants: assimilation efficiency, ingestion rate and efflux rate. For each species a TTF can be derived from laboratory experiments, literature estimates or with greater uncertainty from field data.

Selenium bioaccumulation in sturgeon ($C_{sturgeon}$) is then simply expressed as:

$$C_{sturgeon} = TTF_{sturgeon} * C_{clams}$$

Box 1

$$C_{clams} = K_d * Se_{dissolved} * TTF_{clams}$$

Where:

K_d is a distribution coefficient [L/kg] that describes a relationship between selenium concentrations in particulate and dissolved phases;

C_{clams} represents selenium concentration [μg/g] in sturgeon dietary items and for this computation is conservatively assumed as equal to selenium concentrations in *C. amurensis*

The available TTFs for white sturgeon are regression estimates in the range from 1.0 to 1.7 based on extremely limited data collected in the 1990s (Presser and Luoma 2006). Since then Presser and Luoma (2009) compiled TTFs for fish derived from experimental studies and sets of matching field data and calculated the average TTF for generic fish to be 1.1 and the 75th percentile of 1.34 which also corresponds to the average of the sturgeon TTF range.

Using the default recommended TTF for fish of 1.1 and the typical range of concentrations measured in *C. amurensis* (~5 to 11 µg/g) we can estimate the projected concentration in sturgeon to likely vary from 5.5 to 12.1 µg/g. The upper end of the predicted concentrations is higher that the proposed target range for the TMDL (6 - 8.1 µg/g) and the draft 2004 USEPA criterion of 7.91 µg/g. Yet the above evaluation assumes that sturgeon diet consists entirely of bivalves or includes other food items that have similarly high selenium concentrations and that all selenium is retained by sturgeon. In fact, other components of sturgeon's diet in the North Bay exhibit much lower selenium concentrations from ~ 1 to 3 µg/g (Stewart *et al.* 2004) and there is new evidence to suggest that the diet of white sturgeon may comprise only 40% of *C. amurensis* (T. Presser, USGS, *pers. comm*. May 12, 2010).

Moreover, Poulton and others (2004) investigated spatial and seasonal patterns of clams and found that densities of *C. amurensis* at six sites in San Pablo Bay declined dramatically over winter (mean= 152 m^{-2}) while other clams were still abundant. The highest density among more than 1700 core samples was only 2206 m^{-2} which is far lower than those commonly found in 1987-88 (>10000 individuals per m^{-2}). An approximately 20-fold decline in the bivalve abundance in San Francisco Bay after 1998 has been also linked to the increased predation by Crangon shrimp, juvenile Dungeness crab and English sole which have persisted at high densities since 1999 (Cloern *et al.* 2007).

Therefore, it may be considered that white sturgeon is not exposed to as much selenium in its diet as previously thought. We cautiously assumed that sturgeon's diet includes 50% of *C. amurensis* and thus the selenium dietary intake is approximately 7 µg/g, which is in all likelihood higher than the overall selenium concentration in food items consumed by sturgeon. The subsequent tissue concentrations calculated with the TTF of 1.1 will be in the range of 8 µg/g. A TTF of 1.3 could result in tissue concentrations reaching 9.1 µg/g. In the North Bay-Delta in 2002-09 the mean selenium concentration found in 53 samples of sturgeon muscle was 6.6 µg/g dw (Figure 29). Only 8% of samples collected since 2002 exceeded the upper value of the numeric target range and 9 out of 53 samples had selenium concentrations above 10 µg/g.

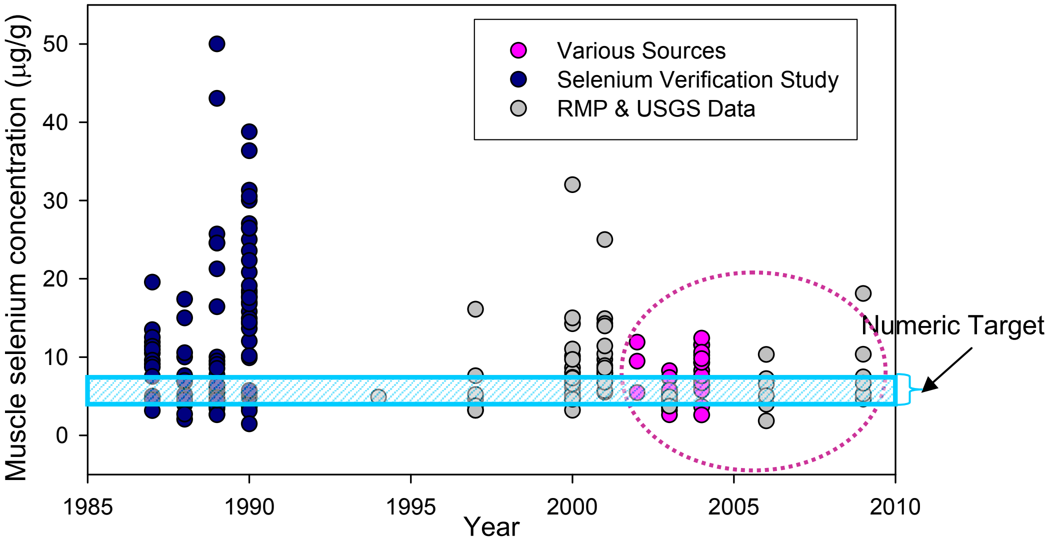


Figure 29: Observed selenium concentrations in white sturgeon in the North Bay

Linking Fish Tissue Target to Water Column Concentrations

Although aqueous selenium concentrations could not be linked directly to bioaccumulation in sturgeon, transformation from dissolved forms to living organisms takes place at the base of the food web and for that reason it has a bearing on the amount of selenium available for higher level predators. In addition, knowing the threshold dissolved selenium concentration in the North Bay that could potentially limit the adverse effects on sturgeon provides means for monitoring these concentrations as part of routine water quality measurements in the Bay and, in the future, could be used to track reductions of selenium due to source control efforts or implementation of best management practices. Water column concentrations can also offer a starting point for an initial risk characterization and assessment.

In the calculation of the water column concentration of selenium from the desired sturgeon tissue concentration of 8.1 µg/g we followed the general approach developed by Presser and Luoma (2009, 2010) that was first used for the San Diego Creek and Newport Bay TMDL (*in preparation*). Table 24 shows methodology steps and the assumptions used in the translation process. By rearranging the equations in ***Box 1*** above, the dissolved selenium ($Se_{dissolved}$ in µg/L) can be calculated as follows:

$$Se_{dissolved} = \frac{C_{sturgeon}}{TTF_{sturgeon} * TTF_{clams} * K_d} * 1000$$

Where: $C_{sturgeon}$ – fish tissue criterion/numeric target

Table 24: Selection of parameters for translation of sturgeon tissue numeric target to water column concentration

Methodology steps	**Assumptions**
Determine the target species	Sturgeon
Choose toxicity guideline (numeric target) for fish	Numeric Target: 6 - **8.1** µg/g
Choose species-specific TTF_{fish} or use default TTF_{fish} of 1.1	$TTF_{generic\ fish}$ = 1.1 $TTF_{sturgeon}$ = **1.3**
Identify appropriate food web(s) for selected fish species based on fish-specific diet	Benthic – dominated by *C. amurensis* Benthic – with a mixed diet of *C. amurensis (50%) and M. balthica (50%)*
Choose TTF_{clams} for invertebrates in selected food web or use default TTF_{clams} for class of invertebrate	$TTF_{C.\ amurensis}$ = range 4.0 – 8.5 => **6.25** $TTF_{M.\ balthica}$ = 4.5
Choose K_d based on source of selenium and receiving water conditions	Computed from modeled data
Translation assuming a single invertebrate diet Translation assuming a mixed invertebrate diet	$C_{water} = (C_{sturgeon}) \div (TTF_{fish})(TTF_{clam})(K_d)$ $C_{water} = (C_{sturgeon}) \div (TTF_{fish})(K_d)$ $[0.5(TTF_{C.amurensis}) + 0.5(TTF_{.M.balthica})]$

Partitioning of selenium between water and particulate material is a dynamic biogeochemical process and the distribution coefficient (K_d) which describes the proportion of selenium associated with particulate matter at any given time and location may vary by many orders of magnitude (Presser and Luoma 2009). In fact, K_d varies more widely than any other parameter used in the translation process and careful consideration should be given while selecting the appropriate values. By definition K_d values greatly depend on selenium speciation in the water column. For translation of sturgeon tissue target to a water column concentration we derived the K_d values from the ECoS3 model simulations of transport and dynamics of different dissolved and particulate selenium species throughout the North Bay.

The modeling results verify that large spatial and temporal variability in selenium partitioning exists, which signifies that even the monitoring data, after all representing instantaneous conditions, may not be adequate to fully describe selenium transformations occurring in a complex ecosystem such as the North Bay. However, the ECoS3-based modeling framework helps establish a first-order understanding of relevant transformation conditions that are linked to specific hydrodynamic regimes and reflective of ecological factors making it especially effective in K_d determination.

The model estimated K_{ds} (particulate/dissolved selenium) at five locations for the period of 1999-2007 were used to compute the K_d statistics. K_d values generally increased from Suisun Bay to San Pablo Bay and to Central Bay, largely as a result of the organic enrichment of particulates that takes place from the riverine boundary to the ocean boundary (Table 25). The calculated K_{ds} range from 2000 to just over 17000 L/kg and are generally within the array of values found in estuaries.

Table 25: Selenium partitioning coefficient (K_d) as a function of location in the North Bay and the North Bay average

	Rio Vista	Suisun Bay	Carquinez Strait	San Pablo Bay	Central Bay	North Bay
MIN	2719	2598	2235	2577	4930	2954
MAX	9461	12059	14634	17214	16541	12785
MEAN	5326	4791	5379	7939	14116	6676
75th Percentile	6145	5373	6606	10111	15301	7581

Although in the North Bay the change in dissolved selenium concentrations is small, the particulate concentrations increase with distance from the Delta resulting in higher values of K_{ds}. These are caused by an increase in the chlorophyll *a* to total suspended material (TSM) ratio across the North Bay. The higher particulate selenium values also appear to result in higher clam concentrations at greater distances from the Delta, where higher salinities offer more favorable habitat conditions. The changing mix of particulate selenium across the North Bay, with increasing proportion of organic selenium, is shown in Figure 30.

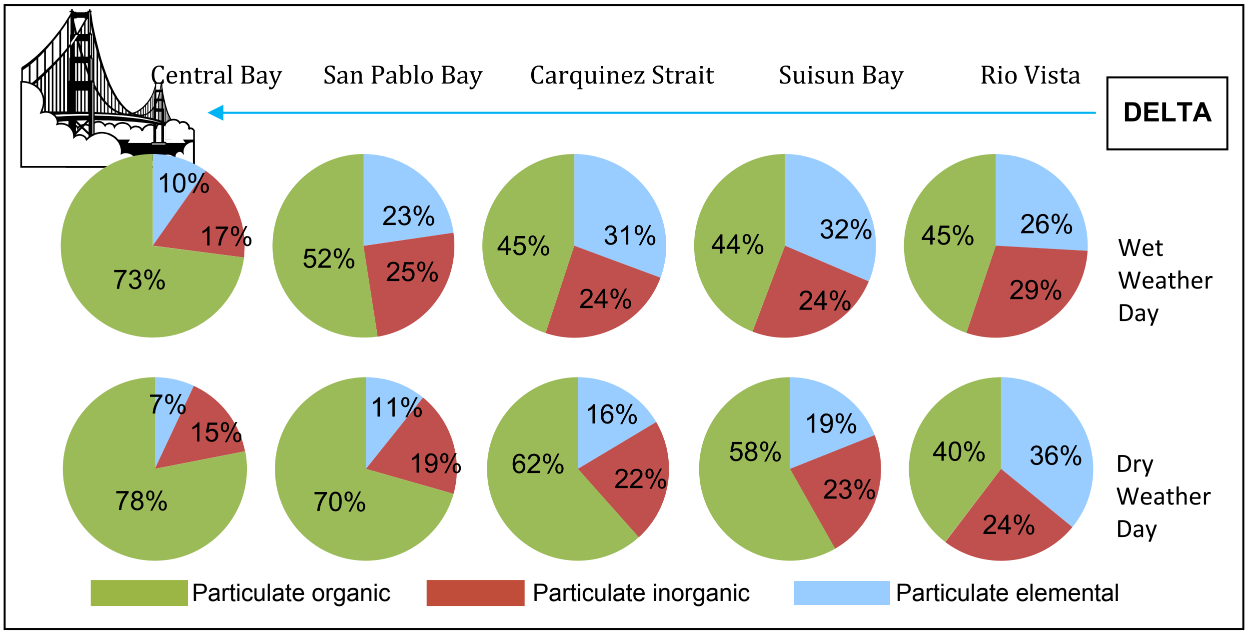


Figure 30: Changing mix of particulate selenium from the Delta to the Golden Gate

Table 26 shows the water column concentrations translated from the upper sturgeon tissue target of 8.1 μg/g for the computed statistics of the K_d values and the TTF values in Table 24. Estimated target concentrations based on mean K_d values and the sturgeon-specific TTF of 1.3 range from 0.21 μg/L in Suisun Bay to 0.07 μg/L in Central Bay with the North Bay–wide concentration of 0.15 μg/L. In random sampling of selenium in the North Bay (2002- 2008) the measured selenium concentrations varied from 0.04 to 0.44 μg/L (75th percentile = 0.125 μg/L) and the mean concentration was 0.10 μg/L. Considering conservative assumptions applied at each step of the target translation process these results tentatively suggest that the North Bay shows signs of at least a limited capacity to assimilate existing selenium loadings.

Table 26: Water column targets corresponding to the sturgeon target of 8.1 μg/g, clam to fish TTF of 1.1 and 1.3 and with clam TTF of 6.25

TTF$_{fish}$ = 1.1		**Rio Vista**	**Suisun Bay**	**San Pablo Bay**	**Central Bay**	**North Bay**
		Dissolved Se concentration [μg/L]				
K_d	MIN	0.43	0.45	0.46	0.24	0.40
	MAX	0.13	0.10	0.07	0.07	0.09
	MEAN	**0.22**	**0.25**	**0.15**	**0.08**	**0.18**
	75th %ile	0.19	0.22	0.12	0.08	0.16

$TTF_{sturgeon}$ = 1.3		Rio Vista	Suisun Bay	San Pablo Bay	Central Bay	North Bay
		Dissolved Se concentration [µg/L]				
K_d	MIN	0.37	0.38	0.39	0.20	0.34
	MAX	0.11	0.08	0.06	0.06	0.08
	MEAN	**0.19**	**0.21**	**0.13**	**0.07**	**0.15**
	75th %ile	0.16	0.19	0.10	0.07	0.13

Knowing that sturgeon like most fish eat a diverse diet comprising at least an assortment of benthic organisms we also constructed a conservative scenario in which 50% of the sturgeon's *C. amurensis* diet is substituted with *Macoma balthica* another invertebrate common in San Francisco Bay and with high selenium TTF of 4.5. Following the translation steps (see Table 24 for assumptions) the allowable water column concentrations in the North Bay segments range from 0.08 to 0.24 µg/L for the estimated average K_d (Table 27). A mean selenium concentration of 0.17 µg/L is predicted as protective of sturgeon when the entire North Bay is considered, which again is higher than the monitored average water column concentration of 0.10 µg/L.

Table 27: Water column targets corresponding to the sturgeon target of 8.1 µg/g, mixed invertebrate diet and clam to fish TTF of 1.3

$TTF_{sturgeon}$ = 1.3		Rio Vista	Suisun Bay	San Pablo Bay	Central Bay	North Bay
		Dissolved Se concentration [µg/L]				
K_d	MIN	0.43	0.45	0.45	0.24	0.40
	MAX	0.12	0.10	0.07	0.07	0.09
	MEAN	**0.22**	**0.24**	**0.15**	**0.08**	**0.17**
	75th %ile	0.19	0.22	0.12	0.08	0.15

Seasonal Variations

The diminishing freshwater inflow from the Delta during dry weather season together with the increasing residence time could amplify the impact of in-the-Bay selenium sources, predominantly discharges from petroleum refineries, on selenium transformations and bioavailability. Therefore, the estimates of target concentrations for dry and wet seasons and different hydrologic regimes are useful to evaluate the linkages between selenium loading and the potential for adverse effects. The results in Table 28 show that for the evaluated set of conditions the water column concentrations would need to be lower during the dry season to reduce the potential for toxic exposure in sturgeon. However, only for the worst case scenario (dry and wet season during a dry year) and the most conservative parameters are the computed target concentrations lower than the average selenium concentration measured in the North Bay of 0.10 µg/L (2002-2008).

To ensure protection of sturgeon from potentially harmful concentrations of selenium in the North Bay we propose that the water column target should be derived using the most conservative TTF_{clam} of 6.25, and TTF_{fish} of 1.3 (Table 28). In addition, based upon the characteristics of sturgeon, its long life-span, long-range and irregular spawning the appropriate spatial scale for assessing the compliance with the proposed target should be the entire North Bay rather than the individual Bay segments.

The clam trophic transfer factor of 6.25 represents the utmost value in the range estimated from laboratory experiments with *C. amurensis* and field data. Also this TTF is used by Presser and Luoma (2010) in the translation of selenium tissue guidelines to allowable dissolved selenium concentration for invertebrate-based food webs in San Francisco Bay. In the most recent study with radiolabeled food Lee and others (2006) measured assimilation and efflux parameters from which the calculated TTF varies from 3.6 to 5.4. Therefore, the TTF of 6.25 applied here is likely to overestimate selenium accumulation in clams providing for a reasonable margin of safety.

Table 28: Water column targets corresponding to wet and dry season and different type of hydrologic year

	TTF_{fish} 1.1 **TTF_{clam} 6.25**	**$\text{TTF}_{sturgeon}$ 1.3** **TTF_{clam} 6.25**	**$\text{TTF}_{surgeon}$ 1.3** **Mixed Diet** **TTF_{clam} 6.25/4.5**
1999 (Average Year)			
Wet Season	0.22	0.18	0.21
Dry Season	0.14	0.12	0.14
2001 (Dry Year)			
Wet Season	0.19	0.16	0.18
Dry Season	0.15	0.13	0.15
2005 (Wet Year)			
Wet Season	0.23	0.19	0.22
Dry Season	0.15	0.12	0.14

Sturgeon in San Francisco Bay are not only exposed to varying dietary concentrations throughout the year but also to different forms of selenium and these conditions are hard to replicate in the laboratory setup. In most studies fish are exposed to the most bioavailable forms of selenium at high concentrations so maximum transfer from diet to tissue would be expected. Our preliminary estimates for dry seasons and a dry year indicate that water column concentrations of 0.12 – 0.16 µg/L are protective of sturgeon. For conservatively assumed mixed diet the water column concentrations during the dry year are 0.15 – 0.18 µg/L. This range of selenium appears to represent a foreseeable ambient concentration in the North Bay governed by mixing of the inflows from Sacramento River with the regional background concentrations of approximately 0.07 µg/L, San Joaquin River with concentrations of 0.2 to 0.5 µg/L and the North Pacific concentrations of 0.06 to 0.2 µg/L (Sugimura *et al.* 1976).

The array of water column concentrations computed with a conceivable range of parameters (Table 26, Table 27, Table 28) illustrates the importance of the values of the key parameters in identifying the targets. It is critical that these are calculated with credible data and/or well calibrated and validated models. Despite the greatly improved understanding of selenium processes and considerable amount of data used to develop the estuary model, in some aspects we had to rely on information more than a decade old. Therefore, additional monitoring data are necessary to validate model simulations for current flow and load conditions and, subsequently, to enhance the level of confidence in the translated water column targets.

Major Uncertainties and Next Steps

During the scientific review process of the modeling framework, crucial data needs and technical limitations were identified and discussed. It was agreed that the issues associated with defining the Sacrament River boundary conditions, riverine loading of organic selenium in phytoplankton and the rates at which different selenium species are converted to organic selenides could not be resolved without additional monitoring and research that may extend beyond the scope of this project.

One of the major concerns identified was lack of selenium particulate data which is essential to better quantify and confirm the role of the background selenium load entering the Bay. The model simulations discussed in Technical Memorandum 6 (Tetra Tech 2010) show that the selected particulate selenium concentrations at the system boundaries (Delta and Golden Gate Bridge) could have a significant effect on the predicted particulate selenium concentrations in the water column which, in turn, is critical to forecasting trophic transfer and bioaccumulation in predators. The modeling results are based on the existing data to characterize the boundary conditions. The lack of particulate selenium concentration measurements in the freshwater sections of Sacramento River (e.g. at Freeport) and in the near-shore area beyond the Golden Gate Bridge is potentially a deficiency which also renders considerations of the appropriate remedial actions challenging.

The two main reasons for addition of data from recently conducted studies and for targeted new data collection are:

- to better understand and quantify the declines in selenium concentrations in bivalves and fish since 1999 and to confirm that selenium levels observed in the North Bay have food web and wildlife impacts
- to improve the accuracy of riverine selenium estimates and to clarify the effect of the background selenium load on conditions in the Bay

Three pertinent sources of data have been identified to accomplish the first purpose. These are: (1) RMP 2009 sport fish status and trends monitoring results; (2) USGS bivalve dataset (1995-2008), and (3) selenium tissue concentrations in archived (1997-2007) Largemouth bass from the Central Valley and Bay Delta. This new information is expected to be available later in 2010.

Systematic review of the additional information will strengthen the overall quality of the available data set and the subsequent findings for the TMDL. It is anticipated that the new data will facilitate verification of species of concern in the North Bay and help confirm that the recently observed decreases in concentrations in bivalves are representative of trends over time. Moreover, the RMP monitoring project will investigate the alternative non-lethal sampling (muscle biopsy) in white sturgeon, vital for implementing the TMDL and conducting future monitoring of this large, long-lived fish.

The second goal will be met when an “effluent and receiving water selenium characterization study” is conducted by the petroleum refineries, as required in their reissued NPDES permits.

The overall requirement of this study is to characterize: (1) the concentrations and speciation of selenium in effluent and receiving water, (2) the variability of selenium in the refinery discharge, (3) the potential for uptake and conversion of selenium to more bioavailable forms, (4) mixing and dilution in the receiving waters. The data collected to fulfill the NPDES permit provisions will include sampling of the freshwater reaches of Sacramento and San Joaquin Rivers and analyses of particulate selenium content. This will not only support the verification of riverine loads but will also be used to fine-tune the estuary model calibration thus enhance the accuracy of model predictions.

By extending the TMDL schedule we also anticipate to take advantage of the new assessment tools and guidelines that are being developed on regional and national scale, such as:

- California-wide selenium wildlife criteria (the interagency effort led by the USEPA Region IX in collaboration with US FWS, USGS and NOAA Fisheries)
- Nation-wide aquatic life criterion for selenium and guidance on how to adopt and implement criteria based on fish tissue concentrations (USEPA)

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