

# Selenium biogeochemistry in the San Francisco Bay estuary: changes in water column behavior

Gregory A. Cutter\*, Lynda S. Cutter

*Department of Ocean, Earth, and Atmospheric Sciences, Old Dominion University, 4600 Elkhorn Ave., Norfolk, VA 23529-0276, USA*

Received 26 December 2003; accepted 15 June 2004

## Abstract

The cycling of dissolved selenium was examined in the North San Francisco Bay estuary using 5 surface water transects from the Pacific Ocean (Golden Gate) to the Sacramento and San Joaquin Rivers, monthly river sampling, and three collections of oil refinery effluents during 1997–2000. By combining these data with earlier results from the mid-1980s, a nearly 16-year record of riverine fluxes, estuarine processes, and anthropogenic inputs was obtained. The Sacramento River concentrations and speciation have remained unchanged over the period, and while the speciation of selenium in the San Joaquin is similar, its dissolved selenium concentrations have decreased by almost one half. More significantly, the concentration of selenium from oil refinery discharges to the mid-estuary has decreased 66% and its speciation changed from one dominated by selenite (66%) to one that is only 14% selenite. This change in refinery effluents occurred while our study was underway, with the result being a pronounced decrease in selenite concentrations (82%), and hence total dissolved selenium, in the mid-estuary. A companion study found that sediment/water exchange is a minor flux to the estuary, and hence selenium inputs from the Sacramento River, as well as refineries during low flow (summer, fall) periods exert major controls on the dissolved selenium behavior in this estuary. Nevertheless, in situ processes associated with organic matter cycling (photosynthesis and respiration) still modify the distributions and internal transformations of dissolved selenium, notably organic selenide.

© 2004 Elsevier Ltd. All rights reserved.

*Keywords:* selenium; dissolved; speciation; estuaries; fluxes; San Francisco Bay

## 1. Introduction

Like many trace elements, selenium can be both essential and toxic to aquatic organisms, with this duality depending on its concentration and chemical form (e.g., Harrison et al., 1988; Ohlendorf, 1989). Moreover, anthropogenic activities such as fossil fuel combustion (e.g., Nriagu and Pacyna, 1988) are increasingly delivering selenium to surface waters (e.g., Cutter, 1993), directing considerable attention to the

behavior of this element in the aquatic environment. Dissolved selenium is found as selenate (SeVI), selenite (SeIV), and organic selenides (Org Se-II) in most waters, while particulate selenium can exist as these forms (i.e., selenate and selenite adsorbed or coprecipitated in particulate phases, particulate organic selenide) and as insoluble elemental selenium. Interestingly, phytoplankton show preferential uptake of dissolved selenite (Harrison et al., 1988; Hu et al., 1996) and organic selenide (Baines et al., 2001), which then affects its entry into the food web. Indeed, lab studies demonstrate that dissolved selenium speciation and its food web transfer are important factors in assessing its adverse biological

\* Corresponding author.

E-mail address: [gcutter@odu.edu](mailto:gcutter@odu.edu) (G.A. Cutter).

effects (Luoma et al., 1992). Nowhere is this more relevant than in estuaries which not only are vital nursery grounds for many species of fish and invertebrates, but also the recipients of anthropogenic inputs of selenium (e.g., Cutter, 1989). The San Francisco Bay estuary provides an excellent example of the interaction between selenium's natural biogeochemical cycling, anthropogenic inputs of the element, and potential effects on the food web.

Because of concerns over the potential input of agricultural runoff waters containing elevated selenium, from 1986 to 1988 Cutter and coworkers (Cutter, 1989; Cutter and San Diego-McGlone, 1990) examined the cycling of selenium and temporal variability of its fluxes in the San Francisco Bay estuary. This estuary (Fig. 1) consists of 2 major river inputs, the Sacramento and San Joaquin Rivers, which then flow into Suisun Bay, Carquinez Strait, San Pablo Bay, Central Bay, and the North Pacific Ocean via the Golden Gate (collectively known as the "North San Francisco Bay"). The South San Francisco Bay is lagoonal in nature since most of its circulation is tidally driven due to minimal freshwater input (primarily effluent from sewage treatment plants and the seasonal Coyote Creek; Conomos et al., 1979;

Walters et al., 1985). Work in the 1980s demonstrated that dissolved selenium was delivered to the northern Bay principally by the Sacramento River and by effluents from oil refineries located in the vicinity of Carquinez Strait (Cutter, 1989; Cutter and San Diego-McGlone, 1990). Significantly, dissolved selenium from refinery discharges was predominantly selenite, in contrast to that from rivers (selenate > organic selenide > selenite; Cutter and San Diego-McGlone, 1990), providing a speciation "signature" for these inputs. Dissolved selenium fluxes from refineries accounted for 50–90% of the total input (Cutter and San Diego-McGlone, 1990) and during low river discharge (summer and fall) mid-estuarine maxima in all selenium species were present (Cutter, 1989). Dissolved selenium behavior during high river discharge (spring) showed a combination of conservative mixing and non conservative input and removal for all chemical species, with river fluxes dominating the inputs, and non conservative processes resulting from phytoplankton uptake and the regeneration of particulate organic selenide in the water column and sediments (Cutter, 1989).

Since the late 1980s, few comprehensive studies of selenium biogeochemistry in the San Francisco Bay

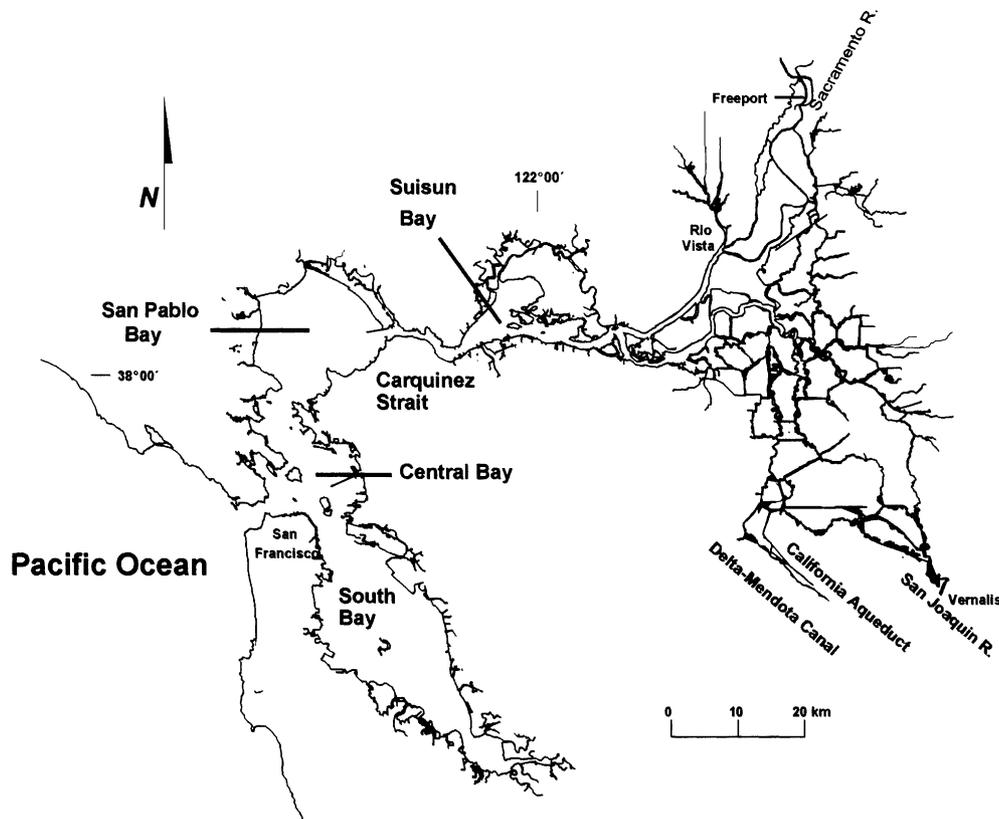


Fig. 1. The San Francisco Bay Estuary study region, extending from the seaward end at the Golden Gate (Bay entrance just north of San Francisco) and through Central Bay, San Pablo Bay, Carquinez Strait, and Suisun Bay to the Sacramento River at Rio Vista. The San Joaquin River flows from the south into the Bay via the complex series of manmade channels, small rivers and streams, wetlands, and diked agricultural fields known as the Delta. The South San Francisco Bay (South Bay) was not sampled during this study.

estuary have been made. However, several compelling reasons for re-examining selenium in this estuary have developed: mandated reductions in selenium discharge from refineries (e.g., CSFBRWQCB, 1992), legislated minimum flows of San Joaquin River into the estuary (1994 Bay–Delta Water Accord; CSWRCB, 1994) which has dissolved selenium concentrations of over 10 times those of the Sacramento River (Cutter and San Diego-McGlone, 1990), and elevated selenium concentrations in the invasive clam, *Potamocorbula amurensis*, that is now the dominant bivalve in the North SF Bay and an important component of the estuarine food web (Alpine and Cloern, 1992; Linville et al., 2002). This paper examines the distribution and fluxes of dissolved selenium species in the North San Francisco Bay, including the San Joaquin and Sacramento Rivers, from 1997 to 2000, with particular emphasis on decadal changes. Two companion papers discuss particulate selenium in North SF Bay's seston and phytoplankton (Doblin et al., submitted for publication), and sediments (Meseck and Cutter, submitted for publication).

## 2. Methods

### 2.1. Field sampling

Estuarine transects of the North SF Bay (Fig. 1) from the Golden Gate to the Sacramento (Rio Vista) and San Joaquin (USGS Station 757) Rivers were made in 5–6 November 1997, 16–17 June 1998, 7–8 October 1998, 13–14 April 1999, and 4–5 November 1999 using the US Geological Survey's (USGS) Research Vessel *Polaris*. These dates were chosen to match those of the earlier studies and because river flow (highest in spring and lowest in fall) is the dominant control on the estuarine behavior of selenium in SF Bay (Cutter, 1989; Cutter and San Diego-McGlone, 1990). Eighteen to 20 stations were occupied on the transects at ca. 1.5 salinity intervals. Water samples were acquired with 5 L Go-Flo bottles deployed on a Kevlar cable and triggered with a plastic messenger 1 m below the surface. After recovery, the bottle was pressurized with 8 psi nitrogen and water directed through a precleaned and tared 142 mm diameter, 0.4  $\mu\text{m}$  polycarbonate membrane held in a Teflon filter holder (filters frozen for TSM analyses; see Doblin et al., submitted for publication). Filtered water was placed in 1 L borosilicate bottles (Teflon-lined caps), acidified to pH 1.6 with HCl, and stored in the dark until analysis for Se speciation. Filtered water was also placed in 125 mL borosilicate bottles for salinity/chlorinity determinations, and 125 mL polyethylene bottles that were immediately frozen for nutrients. In addition, samples were collected for chlorophyll, particulate organic matter, and particulate selenium analyses (see Doblin et al., submitted for publication).

Time series samples for river inputs were taken at Vernalis (37.67°N, 121.27°W) for the San Joaquin River and at Freeport (38.45°N, 121.50°W) on the Sacramento River from January 1998 to September 2000 using a trace metal clean pumping and filtration (0.45  $\mu\text{m}$ ) system. Samples were treated and stored in the same manner as those for the estuarine transects. Three sets of refinery effluent samples were collected from 5 refineries on 13 October 1999, 22 May 2000, and 17 or 22 August 2000. These were from 24 h composite samples and were collected in 2 L polyethylene bottles, returned to the USGS laboratory in Menlo Park, California, vacuum filtered through a 0.45  $\mu\text{m}$  membrane, and the filtrate acidified and treated as above for estuarine or river samples.

### 2.2. Sample analyses

The speciation of dissolved selenium was determined using the selective hydride generation/atomic absorption detection method described by Cutter (1978, 1982, 1983). Briefly, within a glass stripping vessel selenite was quantitatively converted to hydrogen selenide using sodium borohydride addition to a sample containing sulfanilamide (to eliminate interference due to nitrite) and acidified to 4 mol l<sup>-1</sup> HCl. The evolved hydrogen selenide was stripped from solution using helium and trapped in a borosilicate U-tube packed with silanized glass wool and immersed in liquid nitrogen. After the trap was removed from the LN<sub>2</sub>, an atomic absorption spectrometer fitted with an open quartz tube furnace burning an air–hydrogen flame was used to detect the hydride; instrument response (as peak area) was recorded on a chromatographic integrator. To determine selenate + selenite, another acidified sample was boiled for 15 min, cooled, and then subjected to the selenite determination; selenate is the difference between this determination and that of selenite. Total dissolved selenium was determined by boiling a 4 mol l<sup>-1</sup> HCl acidified sample, with the addition of potassium persulfate, and then following the selenite procedure. The difference between total dissolved selenium and selenite + selenate yields the concentration of dissolved organic selenide + elemental selenium (this may be colloidal and pass through the 0.4  $\mu\text{m}$  filter). However, many studies have shown that this fraction is primarily organic selenide in the form of dissolved peptides (Cutter, 1982; Cutter and Bruland, 1984; Cutter and Cutter, 1995), and hereafter it is referred to as “dissolved organic selenide”. To ensure accuracy, all determinations utilized the standard additions method of calibration, and all samples were analyzed in triplicate to quantify precision (found to be <4% for concentrations above 0.4 nmol l<sup>-1</sup>). Detection limits for all three selenium forms was 0.02 nmol l<sup>-1</sup>.

The nutrients phosphate, silicate, and nitrate + nitrite (referred to as “nitrate”) were determined using the colorimetric methods of Parsons et al. (1984), modified for use by an Alpkem rapid flow analyzer. Salinity was determined using a Portasal salinometer with IAPSO standard seawater as the reference.

### 3. Results

#### 3.1. Selenium in the Sacramento and San Joaquin Rivers

By combining the 1997–2000 riverine Se data with those from our earlier studies (July 1984–April 1988; Cutter, 1989; Cutter and San Diego-McGlone, 1990), an excellent record of selenium input to the SF Bay from the Sacramento (Fig. 2) and San Joaquin (Fig. 3) Rivers under various flow regimes was obtained. It is clear that

the concentrations of all selenium species in the Sacramento were remarkably constant over the 16-year period; total dissolved selenium averaged  $0.91 \pm 0.27 \text{ nmol l}^{-1}$  ( $n = 56$ ), while selenate was  $0.45 \pm 0.24 \text{ nmol l}^{-1}$  (47% of total), organic selenide  $0.35 \pm 0.21 \text{ nmol l}^{-1}$  (40% of total), and selenite was  $0.11 \pm 0.08 \text{ nmol l}^{-1}$  (13% of total). These values are essentially identical to concentrations found in the 1980s by Cutter and San Diego-McGlone (1990). However, unlike these previous results, this longer data set shows a poor correlation between river discharge (Fig. 2) and any of the dissolved selenium forms, with selenate vs. discharge having the best correlation ( $r = 0.35$ ). In contrast to the Sacramento, selenium concentrations in the San Joaquin (Fig. 3) were up to 86 times higher, with total dissolved selenium averaging  $15.8 \pm 10.5 \text{ nmol l}^{-1}$  ( $n = 60$ ), selenate  $11.2 \pm 8.5 \text{ nmol l}^{-1}$  (71% of total), organic selenide  $3.56 \pm 3.46 \text{ nmol l}^{-1}$  (23% of total), and selenite averaging  $0.97 \pm 0.75 \text{ nmol l}^{-1}$  (6% of

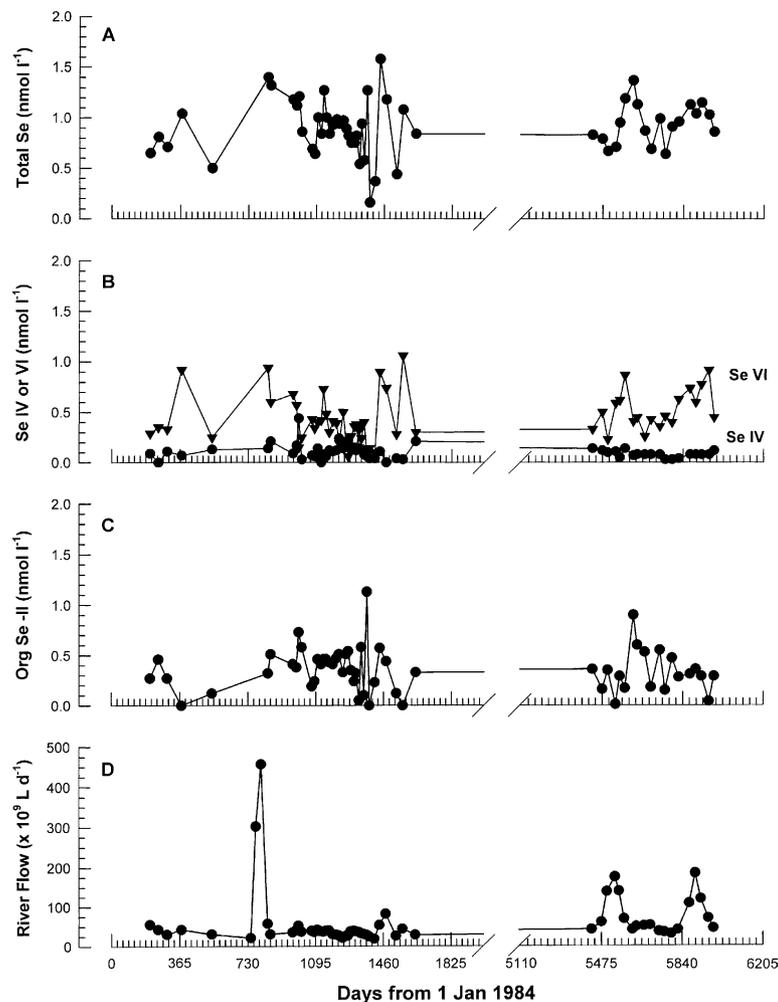


Fig. 2. Selenium in the Sacramento River at Freeport from 1984 to 2000 compiled from data in Cutter (1989), Cutter and San Diego-McGlone (1990), and this work. (A) Total dissolved selenium. (B) Dissolved selenite (Se IV) and selenate (Se VI). (C) Dissolved organic selenide (Se-II). (D) Daily river flow at the sampling times.

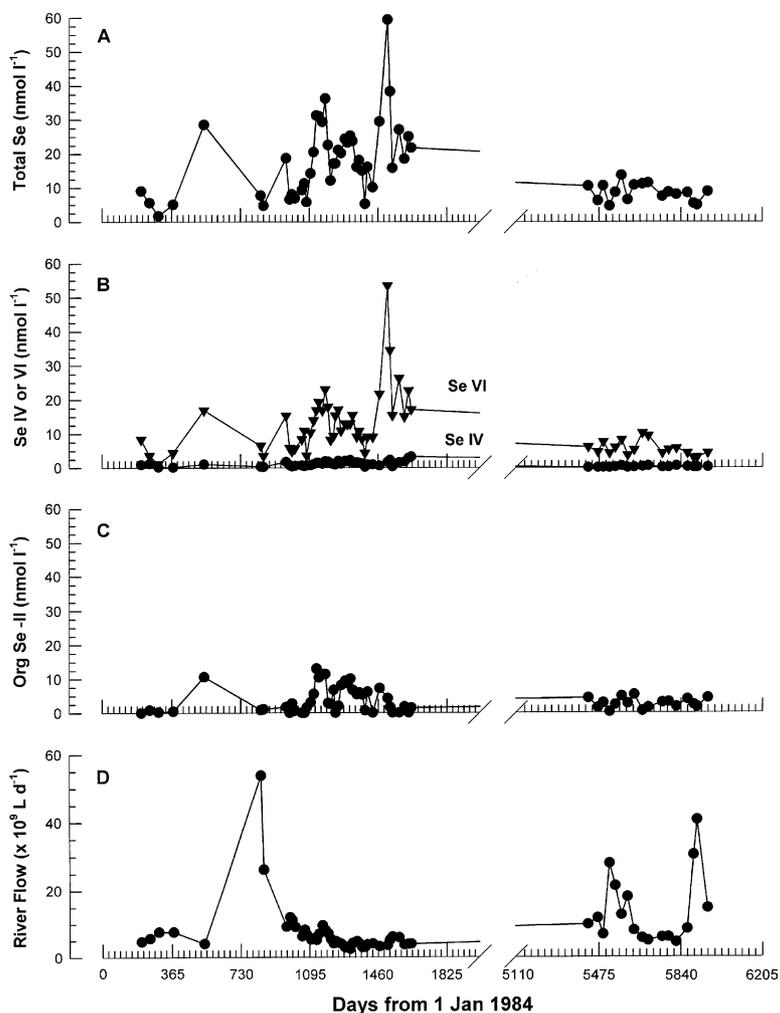


Fig. 3. Selenium in the San Joaquin River at Vernalis from 1984 to 2000 compiled from data in Cutter (1989), Cutter and San Diego-McGlone (1990), and this work. (A) Total dissolved selenium. (B) Dissolved selenite (Se IV) and selenate (Se VI). (C) Dissolved organic selenide (Se-II). (D) Daily river flow at the sampling times.

total) over the 16-year period. These values are slightly lower than those reported earlier (Cutter and San Diego-McGlone, 1990), largely due to the concentration decreases in the last 3 years of observation. Indeed, the 1984–1988 average of total dissolved Se is  $18.5 \pm 11.1 \text{ nmol l}^{-1}$  while the 1997–2000 average is less than half of this value,  $8.6 \pm 2.5 \text{ nmol l}^{-1}$ . Interestingly, dissolved selenium in the San Joaquin correlates better with discharge, but in contrast to the Sacramento, selenite has the best relationship ( $r = 0.42$ ).

The riverine flux of dissolved selenium into the North SF Bay is largely dominated by the Sacramento River, in part because its flow is over 10 times that of the San Joaquin and because export pumping for agricultural and domestic use limits the actual discharge of the San Joaquin into the Delta and North SF Bay (Ball and Arthur, 1979; Cutter, 1989; Cutter and San Diego-McGlone, 1990); this latter factor is anticipated to change in the future since California has required

minimum flows into the Delta (CSWRCB, 1994). Since the Sacramento River selenium concentrations are relatively constant, the flux of dissolved selenium into the North SF Bay then varies with river discharge, less any diverted for agriculture (the so called “Net Delta Outflow Index”, NDOI; California Department of Water Resources). In this manner, the riverine flux of total dissolved selenium to North San Francisco Bay ranged from 4 to  $264 \text{ mol d}^{-1}$ , with an average of  $43 \pm 32 \text{ mol d}^{-1}$ . River fluxes for the 5 estuarine transects are computed in Section 4.1.

### 3.2. Estuarine transects

Since river discharge and the resulting change in freshwater residence time have profound effects on the concentrations and distributions of selenium in the San Francisco Bay (Cutter and San Diego-McGlone, 1990), the classification scheme of Peterson et al.

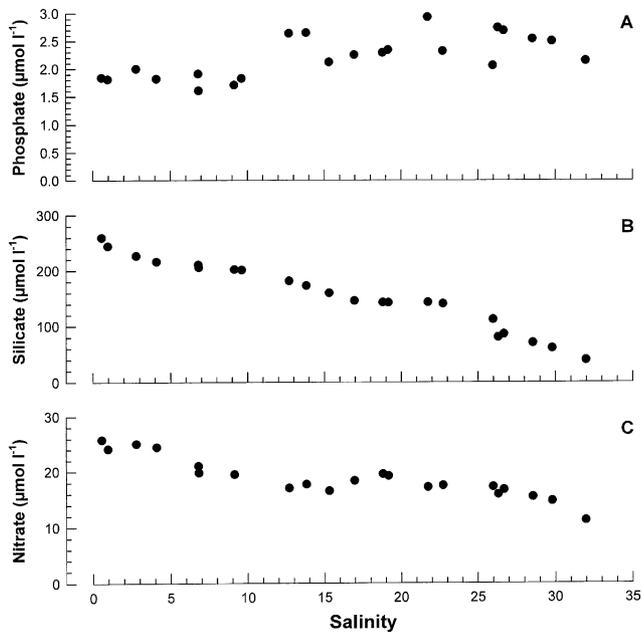


Fig. 4. Estuarine transect data for the dissolved nutrients phosphate (A), silicate (B), and nitrate + nitrite (“nitrate”; C) as a function of salinity in North San Francisco Bay surface waters, 5–6 November 1997.

(1985) into “Wet” (Average NDOI from April to September  $> 3.5 \times 10^{10} \text{ l d}^{-1}$ ), “Intermediate” ( $1.7\text{--}3.5 \times 10^{10} \text{ l d}^{-1}$ ), and “Dry” ( $1.0\text{--}1.7 \times 10^{10} \text{ l d}^{-1}$ ) periods is used as a metric of hydrologic conditions. The first transect in November 1997 occurred during a climatologically Intermediate flow regime (average NDOI =  $2.6 \times 10^{10} \text{ l d}^{-1}$ ), with salinity at the Golden Gate being 32.5. The freshwater residence time (Dyer, 1997) was 68 days and the river input (NDOI) averaged  $1.2 \times 10^{10} \text{ l d}^{-1}$  over this period. Nutrient distributions (Fig. 4) are typical for this season (Peterson et al., 1985) and show phosphate input/regeneration in the mid-estuary (salinity  $> 13$ , Fig. 4A), slight silicate removal in the upper estuary (salinity of 2–5) but otherwise conservative behavior (Fig. 4B), and nitrate removal from salinities of ca. 4–15 (Fig. 4C) where chlorophyll *a* concentrations were slightly elevated (Doblin et al., submitted for publication). Thus, the distributions of nutrients in the estuary in November 1997 were largely controlled by their sources, with phytoplankton uptake and organic matter regeneration exerting only minor effects.

Total dissolved selenium (Fig. 5A) displays an increase going from the river end member (discharge-weighted average of  $2.04 \text{ nmol l}^{-1}$ ) to the mid-estuary (maximum of  $3.0 \text{ nmol l}^{-1}$ ), and then a decrease to the Golden Gate. Selenite (Fig. 5B) displays the same type of distribution (with the exception of 2 anomalously low values in the mid-estuary, increasing from a weighted riverine average of  $0.22 \text{ nmol l}^{-1}$  to a maximum of  $0.9 \text{ nmol l}^{-1}$  at a salinity of 19 (36% of the total), and

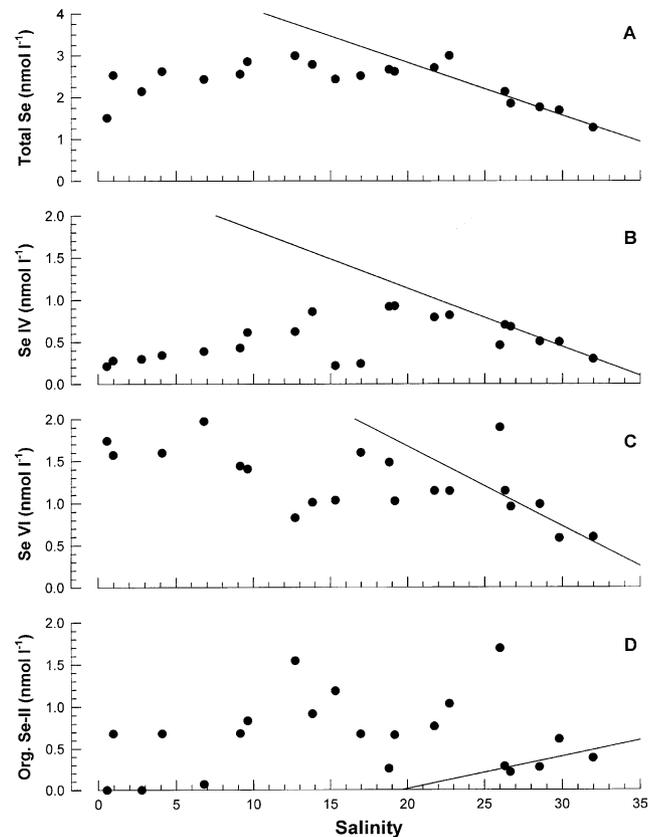


Fig. 5. Dissolved selenium speciation as a function of salinity in surface waters of the North San Francisco Bay on 5–6 November 1997, with straight lines showing linear regression fits to the 5 most seaward data for computing the apparent river end members,  $C_*$ , given in Table 2. (A) Total dissolved selenium ( $r^2 = 0.879$ ). (B) Dissolved selenite ( $r^2 = 0.969$ ). (C) Dissolved selenate ( $r^2 = 0.777$ ). (D) Dissolved organic selenide ( $r^2 = 0.335$ ).

a decrease to  $0.3 \text{ nmol l}^{-1}$  at the Golden Gate. In contrast to selenite, selenate (Fig. 5C) has considerable variability in the estuary, going from an average of  $1.71 \text{ nmol l}^{-1}$  at the rivers to a region of removal (salinity of 7–12) similar to that of nitrate and then input in the mid-estuary (12–26 salinity), followed by a decrease to the Golden Gate. Organic selenide also has considerable variability (river average of  $0.10 \text{ nmol l}^{-1}$ ), but shows two production/input maxima centered at salinities of 13 and 26 (Fig. 5D). Overall, these dissolved nutrient and selenium data are nearly identical to those found in September 1986 under similar river flow conditions (NDOI =  $2.31 \times 10^{10} \text{ l d}^{-1}$  for September 1986; Cutter, 1989), suggesting little change in the processes affecting the concentration and speciation of dissolved selenium over the 11-year interval.

Both of the 1998 transects occurred during climatologically Wet conditions (April–September average NDOI =  $1.4 \times 10^{11} \text{ l d}^{-1}$ ). Indeed, river flows in June were substantially higher than normal (NDOI =  $1.83 \times 10^{11} \text{ l d}^{-1}$ ), lowering the salinity at the Golden Gate to 24.8 and the freshwater residence time to 11

days (similar to April 1986; Cutter, 1989). The nutrient concentrations varied by over 50% in the very low salinities of the upper estuary (Fig. 6A–C), with phosphate and silicate then displaying largely conservative mixing to the Golden Gate, while there may be some nitrate removal starting at a salinity of 5; these results are similar to the Wet years in the Peterson et al. (1985) data set and the very short residence time minimized the effects of phytoplankton uptake. Like the nutrients, concentrations of total dissolved selenium were quite variable at the lowest salinities (Fig. 7A) and discharge weighting the San Joaquin and Sacramento River concentrations yielded an average of  $1.82 \text{ nmol l}^{-1}$ . Considering this end member concentration, it appears that there is an input of total dissolved selenium in the uppermost estuary, but then the distribution is nearly conservative like phosphate and silicate. In contrast to the November 1997 profile, June 1998 selenite concentrations were nearly uniform throughout the estuary (Fig. 7B;  $0.25 \pm 0.08 \text{ nmol l}^{-1}$ ; riverine average was  $0.17 \text{ nmol l}^{-1}$ ), dropping selenite to  $12 \pm 4\%$  of the total for the entire salinity range. Selenate (Fig. 7C) displays an increase in the upper estuary (maximum of  $1.70 \text{ nmol l}^{-1}$ ) from the riverine end member ( $1.19 \text{ nmol l}^{-1}$ ) and a decrease to the seaward end of  $0.96 \text{ nmol l}^{-1}$ ; the observed selenate behavior is quite similar to that in April 1986 (Cutter, 1989). However, the distribution of organic selenide (Fig. 7D) is substantially different than that in April 1986 or November 1997, with a low salinity maximum of  $2.0 \text{ nmol l}^{-1}$  (53% of the total) from the river average of  $0.45 \text{ nmol l}^{-1}$ ,

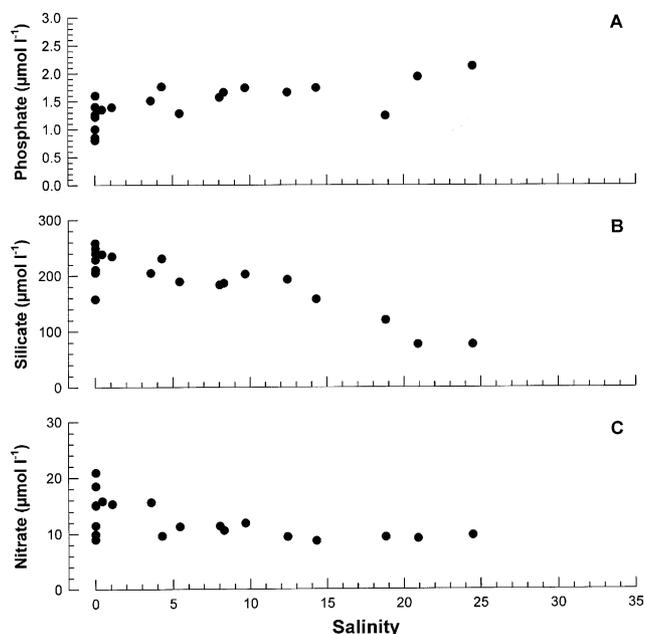


Fig. 6. Estuarine transect data for the dissolved nutrients phosphate (A), silicate (B), and nitrate + nitrite (“nitrate”; C) as a function of salinity in North San Francisco Bay surface waters, 16–17 June 1998.

a rapid decrease into the mid-estuary, and then a slight increase in the Central Bay.

Following the exceptionally high flows of June (all of 1998 were thus considered a Wet year), river discharge to the North SF Bay in October ( $\text{NDOI} = 4.27 \times 10^{10} \text{ l d}^{-1}$ ) was higher than normal and resulted in a salinity of 30.2 at the Golden Gate and a freshwater residence time of 22 days (compare to November 1997). The nutrients show little variation between the two rivers, and thereafter phosphate (Fig. 8A) appears to have mid-estuarine input (9–19 salinity), silicate is largely conservative (Fig. 8B), and nitrate (Fig. 8C) has input in the upper estuary (salinities of 3–6) and removal in the Central Bay (salinities of 24–28). This nitrate removal coincides with an increase in chlorophyll *a* through the San Pablo and Central Bays (Doblin et al., submitted for publication), consistent with phytoplankton uptake (although not likely due to diatoms since silicate was conservative and these species have decreased substantially in the Bay; Lehman, 2000). The dissolved selenium distributions (Fig. 9A–D) show a broad increase for selenite through the Suisun and

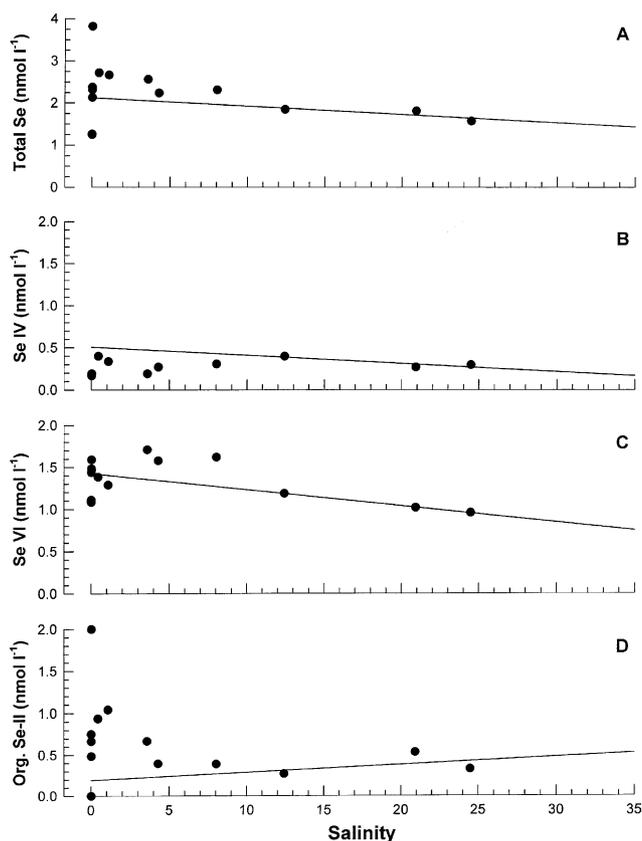


Fig. 7. Dissolved selenium speciation as a function of salinity in surface waters of the North San Francisco Bay on 16–17 June 1998, with straight lines showing linear regression fits to the 3 most seaward data for computing the apparent river end members,  $C^*$ , given in Table 2. (A) Total dissolved selenium ( $r^2 = 0.641$ ). (B) Dissolved selenite ( $r^2 = 0.777$ ). (C) Dissolved selenate ( $r^2 = 0.999$ ). (D) Dissolved organic selenide ( $r^2 = 0.178$ ).

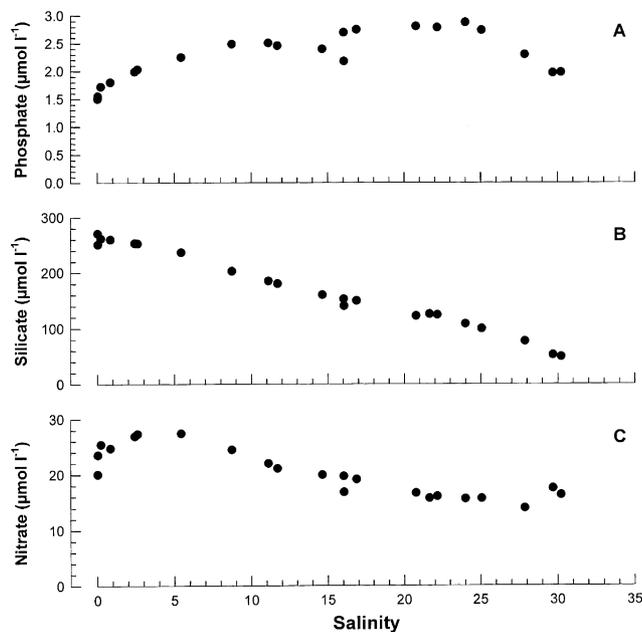


Fig. 8. Estuarine transect data for the dissolved nutrients phosphate (A), silicate (B), and nitrate + nitrite (“nitrate”; C) as a function of salinity in North San Francisco Bay surface waters, 7–8 October 1998.

San Pablo Bays (Fig. 9B) compared to the average river end member ( $0.21 \text{ nmol l}^{-1}$ ), a slight selenate decrease after the river end member ( $1.21 \text{ nmol l}^{-1}$ ; Fig. 9C) and then broad increase like that of selenite. Variable organic selenide concentrations are found in the mid-estuary (Fig. 9D), although both the riverine and seaward end members are quite low ( $0.02$  and  $0.05 \text{ nmol l}^{-1}$ , respectively). Thus, there are no obvious correlations between dissolved Se species, and nutrients and chlorophyll. All these combined yield a total dissolved selenium profile with a broad maximum in the mid-estuary (Suisun and San Pablo Bays; Fig. 9A). In this lower flow period, the most significant features in these profiles are the decreased concentrations of total dissolved selenium, selenite, and selenate compared to the previous year (Fig. 5) or those in September 1986 (Cutter, 1989). However, these decreases are generally over the entire estuary, not in a specific region such as that seen with nitrate (Fig. 8C).

The Peterson et al. (1985) classification scheme places the two final samplings in 1999 during a Wet flow regime (April–September average  $\text{NDOI} = 4.3 \times 10^{10} \text{ l d}^{-1}$ ), although the flow rates dropped rapidly through the summer and fall (see November flow and residence time below). In April the river discharges ( $\text{NDOI} = 9.0 \times 10^{10} \text{ l d}^{-1}$ ) were sufficient to result in a 16-day residence time, only 5 days longer than the high flow June 1998 value, and a salinity of 28.5 at the Golden Gate. Moreover, the upper part of the estuary in Suisun Bay was essentially freshwater, resulting in apparently large nutrient variability near the river inputs (Fig. 10A–C). Proceeding down the estuary, phosphate (Fig. 10A)

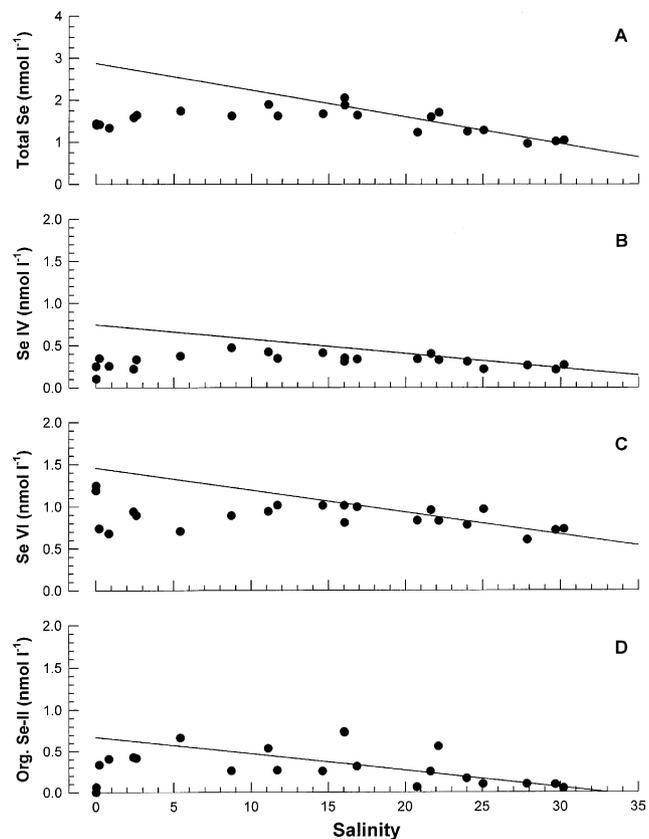


Fig. 9. Dissolved selenium speciation as a function of salinity in surface waters of the North San Francisco Bay on 7–8 October 1998, with straight lines showing linear regression fits to the 5 most seaward data for computing the apparent river end members,  $C_r$ , given in Table 2. (A) Total dissolved selenium ( $r^2 = 0.821$ ). (B) Dissolved selenite ( $r^2 = 0.829$ ). (C) Dissolved selenate ( $r^2 = 0.579$ ). (D) Dissolved organic selenide ( $r^2 = 0.945$ ).

displays the usual increase through the Suisun and San Pablo Bays, while both silicate (Fig. 10B) and nitrate (Fig. 10C) appear to be taken up between salinities of 6–16, with otherwise conservative behavior. There was a large phytoplankton bloom (as reflected in chlorophyll *a* concentrations) throughout the North SF Bay during this sampling and into June 1999 (Doblin et al., submitted for publication; <http://sfbay.wr.usgs.gov/access/wqdata/>), perhaps explaining the observed removal patterns. The selenium results (Fig. 11) are substantially different than the previous observations (Figs. 5, 7, and 9; and Cutter, 1989; Cutter and San Diego-McGlone, 1990), with total dissolved selenium (Fig. 11A) showing a modest mid-estuarine increase from the average riverine end member ( $1.42 \text{ nmol l}^{-1}$ ), very low selenite concentrations (Fig. 11B) being nearly uniform throughout the transect ( $0.19 \pm 0.02 \text{ nmol l}^{-1}$  and only  $14 \pm 4\%$  of the total), and selenate displaying nearly conservative mixing until apparent removal between 16 and 24 salinity (Fig. 11C). This apparent selenate removal does not correspond with that of nitrate. The

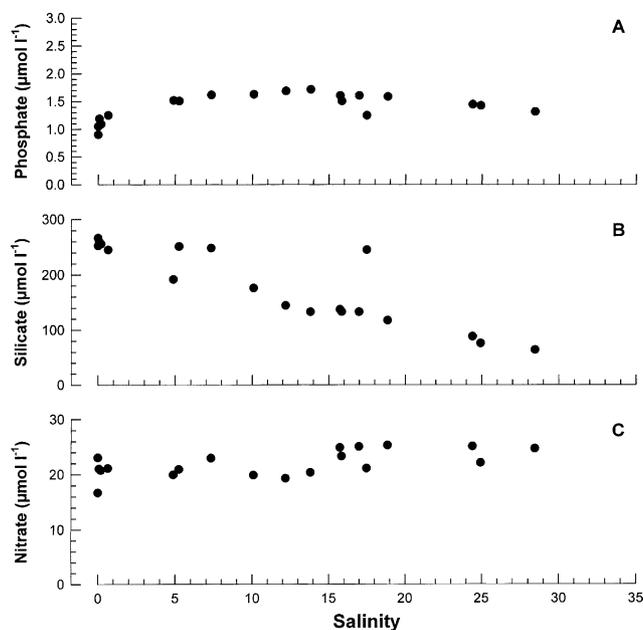


Fig. 10. Estuarine transect data for the dissolved nutrients phosphate (A), silicate (B), and nitrate + nitrite (“nitrate”) as a function of salinity in North San Francisco Bay surface waters, 13–14 April 1999.

estuarine profile of dissolved organic selenide (Fig. 11D) is very much like that of chlorophyll *a* ( $r = 0.44$ ; Doblin et al., submitted for publication) in that it increases into the mid-estuary from the riverine values and remains elevated (40% of total) throughout most of the estuary. Hydrologic conditions in the estuary were nearly identical in April 1986 and 1999, and the 1986 data are plotted in Fig. 11 for direct comparisons. The most notable features are the nearly identical behaviors of selenate and organic selenide (Fig. 11C and D) and the pronounced decrease in selenite and total dissolved selenium (Fig. 11A and B) between these profiles separated by 13 years; this is discussed and quantified below.

The final transect in November 1999 occurred during a rapidly decreasing river flow (October–November average  $\text{NDOI} = 1.1 \times 10^{10} \text{ l d}^{-1}$ ) and the salinity at the Golden Gate (32.2) and freshwater residence time (70 days) are equivalent to those in November 1997. Nevertheless, phosphate only shows minor, if any, increase in the mid-estuary and a rapid decrease in the Central Bay to the Golden Gate (Fig. 12A) compared to 2 years earlier (Fig. 4A), while nitrate has apparent inputs in the mid-estuary and then nearly conservative mixing to the seaward end member (Fig. 12B). The silicate concentrations appear to be anomalously low at the riverine end of the estuary (Fig. 12C) and ignoring these points, display almost conservative mixing similar to the observations of Peterson et al. (1985) and the other fall results given here (Figs. 4C and 8C). The apparent lack of removal is consistent with low chlorophyll concentrations (ca.  $1.2 \mu\text{g l}^{-1}$ ) throughout

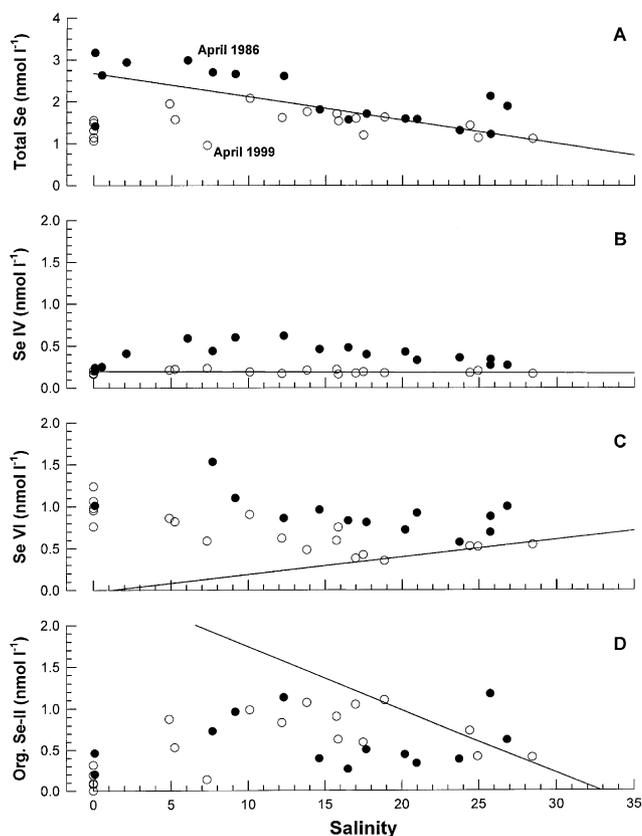


Fig. 11. Dissolved selenium speciation as a function of salinity in surface waters of the North San Francisco Bay on 13–14 April 1999 (open circles) compared to results from 22 to 23 April 1986 (closed circles; Cutter, 1989). For the April 1999 data only, straight lines are plotted to show linear regression fits to the 4 most seaward data for computing the apparent river end members,  $C^*$ , given in Table 2. (A) Total dissolved selenium ( $r^2 = 0.798$ ). (B) Dissolved selenite ( $r^2 = 0.030$ ). (C) Dissolved selenate ( $r^2 = 0.878$ ). (D) Dissolved organic selenide ( $r^2 = 0.847$ ).

all but the Central Bay (where they rose to ca.  $2 \mu\text{g l}^{-1}$ ; Doblin et al., submitted for publication). The November 1999 dissolved selenium results (Fig. 13A–D) have the previously observed pattern of very low and relatively constant selenite concentrations throughout the estuary ( $0.20 \pm 0.03 \text{ nmol l}^{-1}$ , or  $16.0 \pm 3.7\%$  of the total), while total dissolved selenium, selenate, and organic selenide increase from their river end members (0.91, 0.59, and  $0.15 \text{ nmol l}^{-1}$ , respectively) to maxima in the western Suisun Bay, Carquinez Strait, and San Pablo Bay (salinities of 15–26). Thereafter, selenate (Fig. 13C) and total dissolved selenium (Fig. 13A) decrease to the Golden Gate, while organic selenide (Fig. 13D) is relatively uniform in the Central Bay to Golden Gate ( $0.16 \pm 0.07 \text{ nmol l}^{-1}$ ). In general, these fall distributions are similar to those in October 1998 (Fig. 9), but substantially different than the hydrologically equivalent profile taken 13 years previously (September 1986 data in Fig. 13). In 1999, the total dissolved selenium and selenite maxima in the

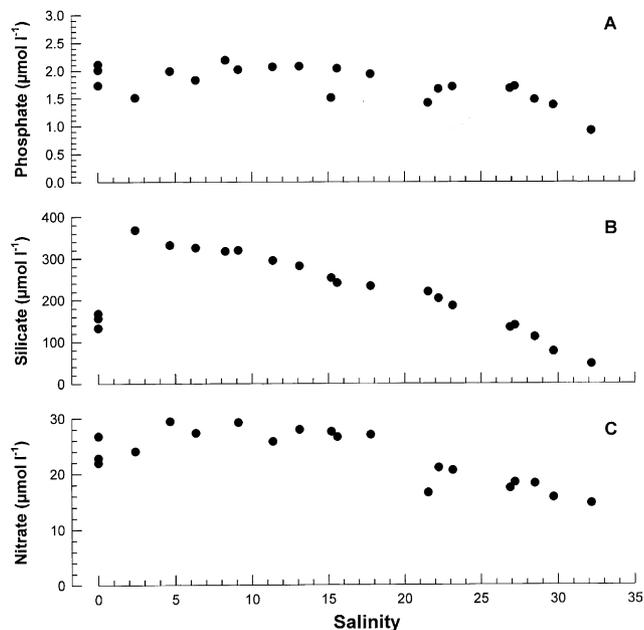


Fig. 12. Estuarine transect data for the dissolved nutrients phosphate (A), silicate (B), and nitrate + nitrite ("nitrate"; C) as a function of salinity in North San Francisco Bay surface waters, 4–5 November 1999.

mid-estuary have disappeared, with selenite dropping from 42% of the total in 1986 to 16% in 1999, and total dissolved selenium in the mid-estuary decreasing 47% between the two periods.

### 3.3. Refinery effluents

Selenium concentrations and speciation for the 1999 and 2000 refinery samples are given in Table 1. Although these concentrations are high relative to the estuarine values, when compared to the refinery data from the 1980s, there are dramatic decreases in concentrations and changes in chemical speciation. When the 1987–1988 data sets (Cutter, 1989; Cutter and San Diego-McGlone, 1990) were combined, total dissolved selenium averaged  $613 \text{ nmol l}^{-1}$  (the range was  $69\text{--}2560 \text{ nmol l}^{-1}$ ) and selenite was 64% of the total on average. In comparison, the average total dissolved selenium for 1999–2000 was  $207 \text{ nmol l}^{-1}$  (Table 1), a 66% decrease, and selenite comprised only 14% of the total. The refinery operations have clearly changed the composition of their effluents and this change appears to have taken place between November 1997 and October 1998 (Figs. 5 and 9). The consequences of these changes are quantitatively examined below, but the simple qualitative consequence of reduced refinery inputs can be seen in the 1986–1999 estuarine comparisons (Figs. 11 and 13); selenite concentrations, particularly in the Suisun Bay–Carquinez Strait–San Pablo Bay region, have decreased by 82% (September 1986–November 1999), roughly the same

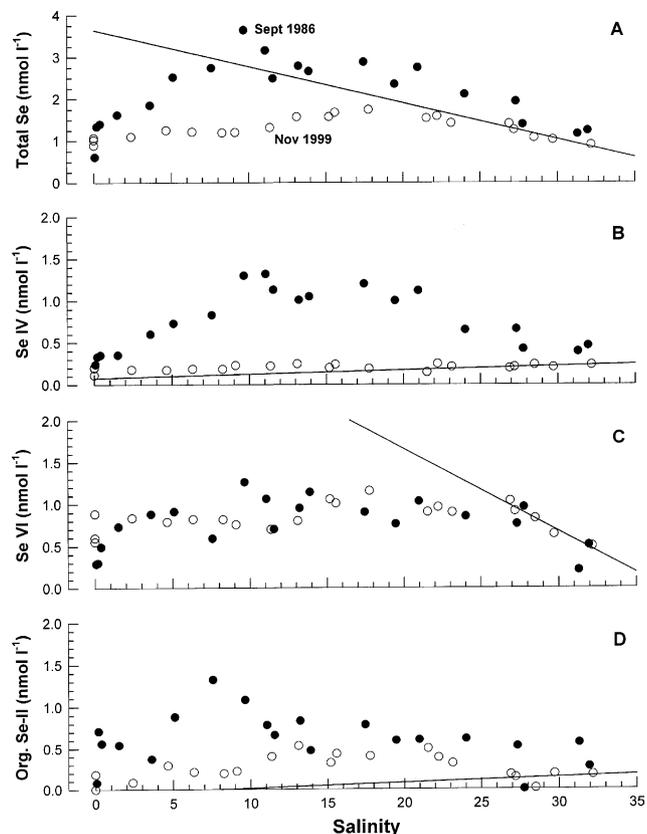


Fig. 13. Dissolved selenium speciation as a function of salinity in surface waters of the North San Francisco Bay on 4–5 November 1999 (open circles) compared to results from 23 to 24 September 1986 (closed circles; Cutter, 1989). For the November 1999 data only, straight lines are plotted to show linear regression fits to the 5 most seaward data for computing the apparent river end members,  $C_*$ , given in Table 2. (A) Total dissolved selenium ( $r^2 = 0.853$ ). (B) Dissolved selenite ( $r^2 = 0.367$ ). (C) Dissolved selenate ( $r^2 = 0.947$ ). (D) Dissolved organic selenide ( $r^2 = 0.037$ ).

decrease (92%) as that in the refinery effluents (assuming that the discharge flow rates have not changed).

## 4. Discussion

### 4.1. Estuarine fluxes

The net fluxes of selenium out of the North San Francisco Bay estuary are the result of external inputs (rivers, refineries, and municipal discharges; note that exchange with the North Pacific Ocean only affects the gross flux) and in situ processes (uptake by primary producers, suspended particulate organic selenium regeneration, and sediment–water exchange). With respect to the latter, previous studies of selenium in SF Bay demonstrated largely conservative behavior for this element. This does not imply that phytoplankton uptake is not taking place or that it does not enter the estuarine food web. Indeed, uptake and movement through the

Table 1  
Dissolved selenium in oil refinery effluents

Refinery	Date	Total Se (nmol l <sup>-1</sup> )	SeIV (nmol l <sup>-1</sup> )	SeVI (nmol l <sup>-1</sup> )	Org Se-II (nmol l <sup>-1</sup> )	R <sup>a</sup> × 10 <sup>6</sup> (l d <sup>-1</sup> )
Chevron	13 Oct 1999	334 ± 10	102 ± 3	217 ± 9	15.0 ± 11.0	19.3
	22 May 2000	38.8 ± 0.2	2.0 ± 0.1	9.5 ± 0.4	27.3 ± 0.4	
	17 Aug 2000	27.0 ± 1.3	0.5 ± 0.01	12.1 ± 0.3	14.1 ± 1.4	
	Average 1987–1988	391	281	61.2	55.2	
Equilon (Shell)	13 Oct 1999	257 ± 6	109 ± 4	156 ± 9	ND	22.4
	22 May 2000	358 ± 13	19.8 ± 0.6	208 ± 4	130 ± 13	
	17 Aug 2000	195 ± 7	60.5 ± 4.0	133 ± 10	ND	
	Shell average 1987–1988	926	636	108	154	
Tosco-Avon	13 Oct 1999	107 ± 1	6.4 ± 0.8	63.9 ± 3.1	36.7 ± 2.7	20.3
	22 May 2000	97.6 ± 6.7	3.4 ± 0.1	20.0 ± 0.7	74.2 ± 6.8	
	21 Aug 2000	51.9 ± 2.0	0.3 ± 0.01	9.0 ± 0.2	42.6 ± 2.1	
	Average 1987–1988	242	69.5	19.8	148	
Tosco-Rodeo (Pacific)	13 Oct 1999	341 ± 4	8.5 ± 0.9	319 ± 1	13.6 ± 4.4	6.7
	22 May 2000	92.4 ± 5.4	0.8 ± 0.1	67.3 ± 3.1	24.4 ± 6.2	
	21 Aug 2000	211 ± 13	1.1 ± 0.0	9.8 ± 0.8	200 ± 13	
	Pacific average 1987–1988	114	54.7	24.6	32.8	
Valero (Exxon)	13 Oct 1999	368 ± 6	23.3 ± 0.7	181 ± 5	164 ± 8	6.8
	22 May 2000	390 ± 16	61.8 ± 0.8	212 ± 10	116 ± 19	
	17 Aug 2000	240 ± 3	31.4 ± 0.8	125 ± 2	83.0 ± 3.6	
	Exxon average 1987–1988	1230	748	41.7	424	

<sup>a</sup> Discharge rate.

food web occur (e.g., Baines et al., 2001; Linville et al., 2002; Purkerson et al., 2003; Doblin et al., submitted for publication), but the biotic removal fluxes are much smaller than the input fluxes, and little effect is observed for dissolved selenium; biotic Se cycling is best studied in the particulate phases (i.e., Doblin et al., submitted for publication). Nevertheless, internal inputs and removals can still be quantified with the dissolved data.

For all but sediment–water exchange, internal selenium fluxes have been previously calculated for the North SF Bay (Cutter, 1989; Cutter and San Diego-McGlone, 1990) and the same methods will be used here for the 1997–1999 data sets covering a range of freshwater residence times (8–70 days). For the 5 estuarine transects, riverine fluxes from the Delta into the estuary ( $F_{riv} = C_0R$ ) were calculated by taking the Sacramento and San Joaquin station concentrations, discharge weighting them (Cutter, 1989), and then recomputing a combined river end member concentration ( $C_0$ ); this was then multiplied by the net freshwater discharge from the Delta ( $R = NDOI$ ). The computed river fluxes are given in Table 2, with the largest value for June 1998 cruise when river discharge was highest. Fluxes out of the estuary ( $F_{est} = C_*R$ ) were estimated by fitting a straight line to the seaward part of the selenium-salinity data and extrapolating the line to salinity = 0 to yield  $C_*$ , the theoretical river end member if only physical mixing of river and sea water were occurring (Cutter, 1989; Cutter and San Diego-McGlone, 1990); these fits are plotted in Figs. 5, 7, 9, 11, and 13. This method assumes minimal effects from riverine end

member variations relative to the estuarine residence time (Officer and Lynch, 1981), a reasonable assumption given the short estuarine residence times and long-period river variations (Figs. 2 and 3; Cutter, 1989); the computed  $F_{est}$  values are listed in Table 2 for each transect. The apparent internal fluxes (positive or negative) are then the difference between  $F_{est}$  and  $F_{riv}$ ; these computations are also found in Table 2.

With three minor exceptions (organic selenide in November 1997 and 1999, and selenate in April 1999; Table 2), the North SF Bay is always a source of dissolved selenium to the North Pacific Ocean, and the total dissolved selenium fluxes are comparable to those in 1986–1988 (Cutter, 1989; Cutter and San Diego-McGlone, 1990). Continuing with total dissolved selenium as an example, the riverine fluxes ( $F_{riv}$  in Table 2) are augmented 17% (June 1998) to 298% (November 1999) by internal inputs ( $F_{int}$ ). However, the components making up total dissolved selenium display a wide variety of behaviors (Figs. 5, 7, 9, 11, 13) and fluxes (Table 2). Therefore, examining the internal fluxes for the individual selenium species can help to reveal processes affecting them. In particular,  $F_{int}$  includes not only in situ biogeochemical processes such as removal via phytoplankton uptake and inputs via organic matter regeneration, but also fluxes from the underlying sediments (Meseck and Cutter, submitted for publication) and point sources such as oil refinery effluents (Table 1) and municipal discharges (Cutter and San Diego-McGlone, 1990). Municipal effluents from sewage treatment plants are primarily in the South San Francisco

Table 2  
Selenium fluxes in the San Francisco Bay estuary

	$C_0$ (nmol l <sup>-1</sup> )	$C^*$	$F_{riv}$	$F_{est}$	$F_{int}$ (mol Se d <sup>-1</sup> )	$F_{refin}$	$F_{sed}^a$
November 1997 ( $R_{avg} = 1.17 \times 10^{10}$ l d <sup>-1</sup> ; $C^*$ calculated at salinity = 32.5)							
Total Se	2.04	5.34	+23.8	+62.3	+38.5	+80.2 <sup>b</sup>	+0.7
SeIV	0.22	2.53	+2.6	+29.5	+26.9	+30.0 <sup>b</sup>	-0.6
SeVI	1.71	3.57	+20.0	+41.6	+21.6	+26.7 <sup>b</sup>	-0.6
Org Se-II	0.10	-0.76	+1.2	-8.9	-10.1	+23.5 <sup>b</sup>	+1.9
June 1998 ( $R_{avg} = 1.83 \times 10^{11}$ l d <sup>-1</sup> ; $C^*$ calculated at salinity = 24.8)							
Total Se	1.82	2.12	+332	+388	+55.4	+51.0 <sup>c</sup>	+0.7
SeIV	0.17	0.51	+31.0	+92.7	+61.7	+12.9 <sup>c</sup>	-0.2
SeVI	1.19	1.42	+217	+260	+42.7	+22.6 <sup>c</sup>	-1.0
Org Se-II	0.45	0.19	+82.2	+35.0	-47.2	+15.5 <sup>c</sup>	+1.9
October 1998 ( $R_{avg} = 4.27 \times 10^{10}$ l d <sup>-1</sup> ; $C^*$ calculated at salinity = 30.2)							
Total Se	1.43	2.87	+61.0	+123	+61.6	+51.0 <sup>c</sup>	+0.7
SeIV	0.21	0.75	+9.0	+32.0	+23.0	+12.9 <sup>c</sup>	-0.4
SeVI	1.21	1.46	+51.4	+62.3	+10.9	+22.6 <sup>c</sup>	-0.8
Org Se-II	0.02	0.67	+0.7	+28.6	+27.9	+15.5 <sup>c</sup>	+1.9
April 1999 ( $R_{avg} = 9.04 \times 10^{10}$ l d <sup>-1</sup> ; $C^*$ calculated at salinity = 28.5)							
Total Se	1.42	2.68	+129	+242	+113	+19.2 <sup>d</sup>	+0.7
SeIV	0.18	0.20	+15.9	+18.1	+2.2	+4.8 <sup>d</sup>	-0.4
SeVI	1.16	0.00	+105	+0.0	-105	+12.3 <sup>d</sup>	-0.8
Org Se-II	0.08	2.50	+7.4	+226	+219	+2.2 <sup>d</sup>	+1.9
November 1999 ( $R_{avg} = 1.07 \times 10^{10}$ l d <sup>-1</sup> ; $C^*$ calculated at salinity = 32.2)							
Total Se	0.91	3.64	+9.8	+39.0	+29.2	+19.2 <sup>d</sup>	+0.7
SeIV	0.13	0.07	+1.4	+0.7	-0.7	+4.8 <sup>d</sup>	-0.3
SeVI	0.59	3.62	+6.3	+38.8	+32.5	+12.3 <sup>d</sup>	-0.9
Org Se-II	0.15	0.00	+1.6	+0.0	-1.6	+2.2 <sup>d</sup>	+1.9

<sup>a</sup> Computed from fluxes in Meseck and Cutter (submitted).

<sup>b</sup> Reported total Se discharge, then subdivided based on 1987–1988 speciation.

<sup>c</sup> Reported total Se discharge, then subdivided based on 1999 (Table 1) speciation.

<sup>d</sup> Calculated from data in Table 1.

and Central Bays, and would therefore only indirectly affect fluxes in the North SF Bay where the data suggest most input occurring from the San Pablo to Suisun Bays. Of the dissolved selenium species, organic selenide fluxes (Table 2) have the largest variability, and for 3 of the 5 transects the internal fluxes are negative, indicating biological uptake (e.g., Baines et al., 2001), oxidation to selenite (Cutter, 1982; Cutter and Bruland, 1984), or diffusion into Bay sediments. Porewater data (Meseck and Cutter, submitted for publication) discount the latter, and in fact sediments are a small source of dissolved organic selenide to the water column (Table 2). The oxidative loss is difficult to evaluate since selenite also has a source from refineries, but the June 1998 organic selenide loss (Fig. 7) can, in addition to refinery flux, explain much of the selenite increase (Fig. 7; Table 2). This leaves biological uptake, in spite of the fact that most organic selenide in marine system appears to be relatively unavailable (e.g., Cutter and Bruland, 1984; Cutter and Cutter, 1998). In terms of the identities of positive organic selenide fluxes (October 1998 and April 1999), refinery effluents and sediment fluxes account for 2–62% of the internal input, so the remainder must be in situ regeneration from particulate organic selenide (Cutter, 1982; Doblin et al., submitted for publication).

Interestingly, the extremely large internal flux in April 1999 occurred during a large phytoplankton bloom throughout most of the North SF Bay (Doblin et al., submitted for publication).

Selenite presents a contrast to organic selenide since it is always “produced” in the estuary (the negative  $F_{int}$  in November 1999 is probably insignificant considering the potential errors). Even though  $F_{refin}$  values decline from 1997 to 1999, refinery effluents can still explain 50–100% of these internal selenite fluxes. The remaining selenite production term, organic selenide oxidation, was only quantified in June 1998 (as discussed above), but otherwise this route is difficult to assess in an estuary with multiple selenite sources. With regards to selenite removal, oxidation to selenate is extremely slow ( $10^3$  years; Cutter and Bruland, 1984) and fluxes into the Bay sediments (Meseck and Cutter, submitted for publication; Table 2) are minor. Since refineries dominate the input of selenite in SF Bay, it is difficult to detect phytoplankton uptake even though it has the highest phytoplankton uptake rates of all the selenium forms (Hu et al., 1996). This detection problem is analogous to being able to observe silicate uptake by diatom blooms in an estuary with very large riverine inputs (e.g., spring phytoplankton blooms in Figs. 6 and 10).

Selenate undergoes many of the same processes that affect selenite and in this respect dissolved selenium in refinery effluents became predominantly selenate by 1998. This results in the internal inputs of selenate also being controlled by refinery fluxes (38–100%), particularly in the late fall under low river discharge. Older data for municipal outflows (Cutter and San Diego-McGlone, 1990) suggest a potentially large source, but this only would have been manifested in the Central Bay where there is little evidence of selenate inputs (typically the 3 highest salinity points in Figs. 5, 7, 9, 11, 13). Selenate fluxes to the sediments are very small (Meseck and Cutter, submitted for publication; Table 2) and although the uptake of selenate by phytoplankton should be slow, especially in the presence of selenite (Hu et al., 1996), the April 1999 data (Fig. 11C) suggest selenate uptake during a large phytoplankton bloom; a similar observation was made in April 1986 (Cutter, 1989). Such selenate depletion is found in open ocean surface waters where selenite is  $<0.10 \text{ nmol l}^{-1}$  and organic selenide appears to be refractory (not bioavailable; Cutter and Bruland, 1984).

## 5. Conclusions

The 1997–1999 data for selenium in the North San Francisco Bay present a stark contrast to those found 10–13 years earlier when selenite was 30–50% of the dissolved inventory of selenium and could be traced primarily to refinery inputs. Indeed, refinery fluxes exceeded those from the rivers during the low flow summer–fall months in 1986–1988 (Cutter, 1989; Cutter and San Diego-McGlone, 1990). The present day refinery fluxes seldom exceed the riverine inputs, are largely selenate, and the few data presented here suggest that the refinery inputs have decreased even further (i.e., Table 1, 1999 vs. 2000 data). As a consequence, selenate and organic selenide are now the predominant forms of dissolved selenium, although the latter undergoes considerable cycling within the estuary and may not be transferred from the SF Bay to the Pacific Ocean. During this period of substantial changes in dissolved selenium, the phytoplankton community has been changing (decreasing diatom and increasing green and bluegreen algae and flagellated phytoplankton species; Lehman, 2000). The removal of phytoplankton has also increased dramatically over the period due to benthic grazing by the invasive clam *Potamocorbula amurensis*, lowering the total phytoplankton biomass (Alpine and Cloern, 1992). No easily quantifiable effects on dissolved selenium are apparent from these biotic changes (fluxes driven by changes in inputs), but there may be effects on the behavior of particulate selenium (Doblin et al., submitted for publication) and selenium in the estuarine

ecosystem (Meseck, 2002; Meseck and Cutter, manuscript in preparation).

Overall, the selenium cycle in the San Francisco Bay estuary has undergone a dramatic change in a relatively short time frame, largely due to changes in refinery operations. This presents an interesting challenge to forecast what future changes will be manifested in the estuary. Its sediments are not a large repository for particulate selenium or fluxes of dissolved selenium to the water column (Meseck and Cutter, submitted for publication; Table 2), leaving a system that is dominated by riverine inputs (Table 2). However, if flows of the San Joaquin River to the SF Bay increase, as suggested by recent legislation (CSWRCB, 1994), the 8–85 fold higher selenium concentrations in this river compared to the Sacramento will likely raise dissolved selenium levels in the estuary. Although this river is dominated by selenate, future studies should evaluate the potential effects of this input to an estuarine system that quickly responds to changes in selenium fluxes.

## Acknowledgements

This project was supported by funds from the NSF EGB Program (OCE-9707946 to G. Cutter) and CALFED (98-2015000-00096). We thank S. Meseck and M. Doblin for sampling and analytical assistance, R. Stewart of USGS for the acquisition and processing of refinery samples, and USGS personnel for river samples. We also thank the captain and crew of the RV *Polaris* for their assistance in sample collection.

## References

- Alpine, A.E., Cloern, J.E., 1992. Trophic interactions and direct physical effects control phytoplankton biomass and production in an estuary. *Limnology and Oceanography* 37, 946–955.
- Baines, S.B., Fisher, N.S., Doblin, M.A., Cutter, G.A., 2001. Uptake of dissolved organic selenides by marine phytoplankton. *Limnology and Oceanography* 46, 1936–1944.
- Ball, M.E., Arthur, J.F., 1979. Planktonic chlorophyll dynamics in the northern San Francisco Bay and Delta. In: Conomos, T.J. (Ed.), *San Francisco Bay: the Urbanized Estuary*. AAAS, Washington, DC, pp. 265–286.
- California San Francisco Bay Regional Water Quality Control Board (CSFBRWQCB), 1992. Mass emissions reduction strategy for selenium. Oakland, California, 53 pp., 1 appendix.
- California State Water Resources Control Board (CSWRCB), 1994. Water quality control plan for the San Francisco Bay/Sacramento–San Joaquin Delta estuary. Sacramento, California, 45 pp.
- Conomos, T.J., Smith, T.E., Peterson, D.H., Hager, S.W., Schemel, L.E., 1979. Processes affecting seasonal distributions of water properties in the San Francisco Bay estuarine system. In: Conomos, T.J. (Ed.), *San Francisco Bay: The Urbanized Estuary*. AAAS, Washington, DC, pp. 115–142.
- Cutter, G.A., 1978. Species determination of selenium in natural waters. *Analytica Chimica Acta* 98, 59–66.

- Cutter, G.A., 1982. Selenium in reducing waters. *Science* 217, 829–831.
- Cutter, G.A., 1983. Elimination of nitrite interference in the determination of selenium by hydride generation. *Analytica Chimica Acta* 149, 391–394.
- Cutter, G.A., 1989. The estuarine behavior of selenium in San Francisco Bay. *Estuarine, Coastal and Shelf Science* 28, 13–34.
- Cutter, G.A., 1993. Metalloids in wet deposition on Bermuda: concentrations, sources, and fluxes. *Journal of Geophysical Research* 98, 16777–16786.
- Cutter, G.A., Bruland, K.W., 1984. The marine biogeochemistry of selenium: a re-evaluation. *Limnology and Oceanography* 29, 1179–1192.
- Cutter, G.A., Cutter, L.S., 1995. Behavior of dissolved antimony, arsenic, and selenium in the Atlantic Ocean. *Marine Chemistry* 49, 295–306.
- Cutter, G.A., Cutter, L.S., 1998. Metalloids in the high latitude North Atlantic: sources and internal cycling. *Marine Chemistry* 61, 25–36.
- Cutter, G.A., San Diego-McGlone, M.L.C., 1990. Temporal variability of selenium fluxes in the San Francisco Bay. *Science of the Total Environment* 97, 235–250.
- Doblin, M.A., Baines, S.B., Cutter, L.S., Cutter, G.A., submitted for publication. Selenium biogeochemistry in the San Francisco Bay estuary: seston and phytoplankton. *Estuarine, Coastal and Shelf Science*.
- Dyer, K., 1997. *Estuaries: a Physical Introduction*, second ed. Wiley, Chichester, pp. 165–166.
- Harrison, P.J., Yu, P.W., Thompson, P.A., Price, N.M., Phillips, D.J., 1988. Survey of selenium requirements in marine phytoplankton. *Marine Ecology Progress Series* 47, 89–96.
- Hu, M., Yang, Y., Martin, J.M., Yin, K., Harrison, P.J., 1996. Preferential uptake of Se(IV) over Se(VI) and the production of dissolved organic Se by marine phytoplankton. *Marine Environmental Research* 44, 225–231.
- Lehman, P.W., 2000. The influence of climate on phytoplankton community biomass in San Francisco Bay Estuary. *Limnology and Oceanography* 45, 580–590.
- Linville, R.G., Luoma, S.N., Cutter, L.S., Cutter, G.A., 2002. Increased selenium threat as a result of invasion of the exotic bivalve *Potamocorbula amurensis* into the San Francisco Bay-Delta. *Aquatic Toxicology* 57, 51–64.
- Luoma, S.N., Johns, C., Fisher, N.S., Steinberg, N.A., Oremland, R.S., Reinfelder, J.R., 1992. Determination of selenium bioavailability to a benthic bivalve from particulate and solute pathways. *Environmental Science and Technology* 26, 485–491.
- Meseck, S.L., 2002. Modeling the biogeochemical cycle of selenium in the San Francisco Bay. PhD dissertation, Old Dominion U., 249 pp.
- Meseck, S.L., Cutter, G.A., submitted for publication. Selenium biogeochemistry in the San Francisco Bay estuary: sediment cycling. *Estuarine, Coastal and Shelf Science*.
- Nriagu, J.O., Pacyna, J.M., 1988. Quantitative assessment of worldwide contamination of air, water and soils by trace metals. *Nature* 333, 134–139.
- Officer, C.B., Lynch, D.R., 1981. Dynamics of mixing in estuaries. *Estuarine, Coastal and Shelf Science* 12, 525–533.
- Ohlendorf, H., 1989. Bioaccumulation and effects of selenium on wildlife. In: Jacobs, L.W. (Ed.), *Selenium in Agriculture and the Environment*. Soil Science Society of America, Wisconsin, pp. 137–177.
- Parsons, T.R., Maita, Y., Lalli, C.M., 1984. *A Manual of Chemical and Biological Methods for Seawater Analysis*. Pergamon, Oxford, pp. 3–33.
- Peterson, D.H., Smith, R.E., Hager, S.W., Harmon, D.D., Herndon, R.E., Schemel, L.E., 1985. *Hydrobiologia* 129, 37–58.
- Purkerson, D.G., Doblin, M.A., Bollens, S.M., Luoma, S.N., Cutter, G.A., 2003. Selenium in San Francisco Bay zooplankton: possible effects of hydrodynamics and food web interactions. *Estuaries* 26, 956–969.
- Walters, R.A., Cheng, R.T., Conomos, T.J., 1985. Time scales of circulation and mixing processes of San Francisco Bay waters. *Hydrobiologia* 129, 13–36.