

# Increased selenium threat as a result of invasion of the exotic bivalve *Potamocorbula amurensis* into the San Francisco Bay-Delta

Regina G. Linville <sup>a,1</sup>, Samuel N. Luoma <sup>a,\*</sup>, Lynda Cutter <sup>b</sup>,  
Gregory A. Cutter <sup>b</sup>

<sup>a</sup> US Geological Survey, 345 Middlefield Road, Mail Stop 465, Menlo Park, CA 94025, USA

<sup>b</sup> Department of Ocean, Earth, and Atmospheric Sciences, Old Dominion University, 4600 Elkhorn Ave., Norfolk, VA 23529-0276, USA

Received 23 February 1999; received in revised form 3 April 2001; accepted 10 October 2001

---

## Abstract

Following the aggressive invasion of the bivalve, *Potamocorbula amurensis*, in the San Francisco Bay-Delta in 1986, selenium contamination in the benthic food web increased. Concentrations in this dominant (exotic) bivalve in North Bay were three times higher in 1995–1997 than in earlier studies, and 1990 concentrations in benthic predators (sturgeon and diving ducks) were also higher than in 1986. The contamination was widespread, varied seasonally and was greater in *P. amurensis* than in co-occurring and transplanted species. Selenium concentrations in the water column of the Bay were enriched relative to the Sacramento River but were not as high as observed in many contaminated aquatic environments. Total Se concentrations in the dissolved phase never exceeded 0.3 µg Se per l in 1995 and 1996; Se concentrations on particulate material ranged from 0.5 to 2.0 µg Se per g dry weight (dw) in the Bay. Nevertheless, concentrations in *P. amurensis* reached as high as 20 µg Se per g dw in October 1996. The enriched concentrations in bivalves (6–20 µg Se per g dw) were widespread throughout North San Francisco Bay in October 1995 and October 1996. Concentrations varied seasonally from 5 to 20 µg Se per g dw, and were highest during the periods of lowest river inflows and lowest after extended high river inflows. Transplanted bivalves (oysters, mussels or clams) were not effective indicators of either the degree of Se contamination in *P. amurensis* or the seasonal increases in contamination in the resident benthos. Se is a potent environmental toxin that threatens higher trophic level species because of its reproductive toxicity and efficient food web transfer. Bivalves concentrate selenium effectively because they bioaccumulate the element strongly and lose it slowly; and they are a direct link in the exposure of predaceous benthivore species. Biological invasions of estuaries are increasing worldwide. Changes in ecological structure and function are well known in response to invasions. This study shows that changes in processes such as cycling and effects of contaminants can accompany such invasions. © 2002 Published by Elsevier Science B.V.

---

\* Corresponding author. Tel.: +1-650-329-4481; fax: +1-650-329-4545.

E-mail address: [snluoma@usgs.gov](mailto:snluoma@usgs.gov) (S.N. Luoma).

<sup>1</sup> Present address: University of California at Davis, Davis, CA, USA.

*Keywords:* *Potamocorbula amurensis*; Selenium; Exotic bivalve

---

## 1. Introduction

Selenium is an environmental toxicant that has been responsible for adverse reproductive effects and local extinctions of fish and birds in cooling reservoirs of coal-fired power plants (Lemly, 1985), wetlands receiving agricultural drainage (Presser and Ohlendorf, 1987; Skorupa, 1998) and river ecosystems draining seleniferous agricultural lands (e.g. the Colorado River and its tributaries; Hamilton, 1999). Although selenium is nutritionally essential, the window is narrow between essential concentrations in food and concentrations that cause adverse effects (Hodson and Hilton, 1983). Selenium becomes a reproductive toxin at slightly enriched concentrations because it substitutes for sulfur in the tertiary structures of proteins and thereby causes deformities in embryos or inhibition of the hatchability of eggs (e.g. Stadtman, 1974; Diplock, 1976; Skorupa, 1998).

Assessment of selenium effects in aquatic systems is complicated by the differing bioavailability of its several oxidation states (VI, selenate; IV, selenite; 0, elemental selenium; -II, selenide) and the occurrence of organic or inorganic forms within an oxidation state (Cutter and Bruland, 1984; Cutter, 1989). Biogeochemical conversion of dissolved Se to particulate forms is also complicated. Organic selenide is produced by plants (such as phytoplankton) or other primary producers (Wrench, 1978; Wrench and Measures, 1982) after uptake of selenite or selenate. Particulate elemental selenium is produced via dissimilatory reduction of selenate or selenite by bacteria (Oremland et al., 1990). Particulate selenium is a critically important phase because diet is the primary route of selenium exposure for invertebrates and other animals (Lemly, 1985; Luoma et al., 1992). Bivalves are especially effective bioaccumulators of selenium because they assimilate almost all the selenium they ingest with particulate material (e.g. from phytoplankton; Luoma et al., 1992) and they lose the element slowly (rate constants of loss are 0.01–0.03 per day; Reinfelder et al.,

1997). The selenium bioaccumulated by invertebrate consumers like bivalves is efficiently transferred to their predators upon ingestion and concentrations can be biomagnified in predator tissues. Therefore, selenium most seriously threatens upper trophic level birds and fish (Lemly, 1995).

Although predators are the species of greatest concern with regard to selenium contamination, they are mobile, impractical to sample in large numbers, and generally not especially useful for routine monitoring. Consumer species like bivalves are practical to sample (Phillips and Rainbow, 1993), and they integrate the influences of environmental concentrations, speciation and transformation of selenium. Bioaccumulated selenium in consumers is the critical link in exposure of predators. Monitoring contaminant exposure in a bioindicator is not a substitute for other types of investigations, but it can help focus more complicated studies of fate and effects (Brown and Luoma, 1995).

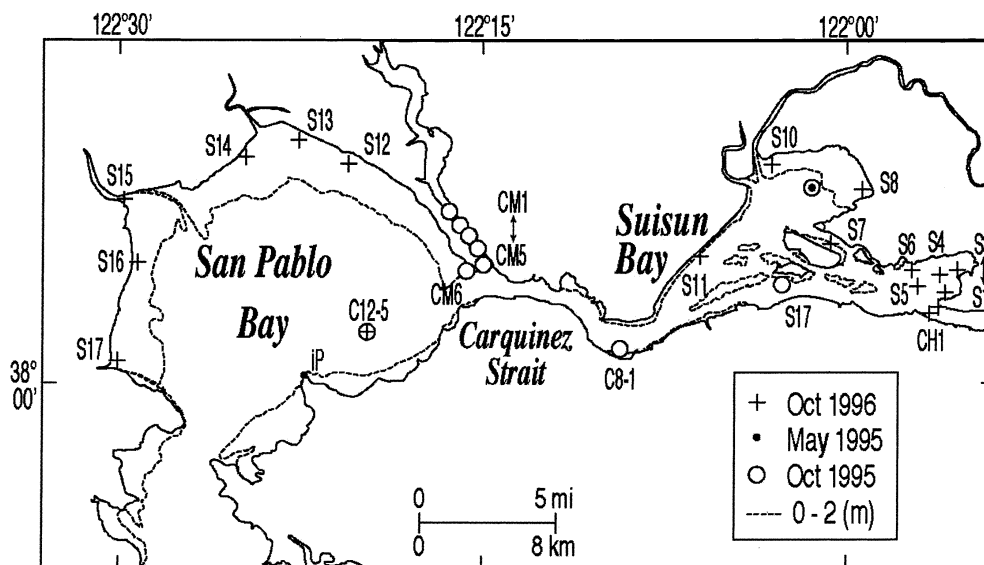
San Francisco Bay, the largest estuary on the west coast of North America, is formed by the confluence of the Sacramento River and the San Joaquin River. The North Bay extends from the confluence of the two rivers to the Golden Gate, and is comprised of Suisun Bay toward the rivers, an intermediate, large and shallow San Pablo Bay, and Central Bay seaward (Fig. 1). The largest water management system in the world can divert 30% of the Sacramento River during high flows and 60% during the low flow season before it reaches the Bay (for agriculture and drinking water; Nichols et al., 1986). Nearly all of the San Joaquin River is recycled southward for agricultural/urban uses by the water management system, during most months, especially in dry years. Wide seasonal and year-to-year changes in freshwater inflow are linked to precipitation and water management (Nichols et al., 1986). Seasonal and year-to-year differences in river inflows control hydraulic residence times in Suisun Bay, the salinity gradient, and distributions of dissolved and

particulate constituents like selenium (Largier, 1996; Monismith et al., 1996; Nichols et al., 1986).

San Francisco Bay is one of the few estuaries in which selenium contamination has been studied (Cutter, 1989; Johns et al., 1988). In the 1980s concentrations of selenium in birds, fish (White et al., 1988; Urquhart and Regalado, 1991) and invertebrates (Johns et al., 1988) in the Bay were high enough to be of concern (Luoma et al., 1992), despite relatively low concentrations of selenium in water (Cutter, 1989). Refineries were the predominant source of selenium during this period, especially during the season of low river discharge (Cutter and San Diego-McGlone, 1990). Saline soils rich in selenium are common in the western San Joaquin Valley (SJV). Release of selenium is accelerated by irrigation of those soils and disposal of irrigation drainage has contaminated ground water, wetlands and riverine habitats in the SJV (Presser and Ohlendorf, 1987). Selenium contamination in the San Joaquin River is well known (Presser and Ohlendorf, 1987); and San Joaquin River inputs could be a source of selenium when waters from that river reach the Bay. The selenium studies of the 1980s showed little input from this source, but those studies were conducted during a prolonged drought when

little runoff from the San Joaquin River reached the Bay.

The purpose of the present paper is to contrast Se contamination in the water column and in bivalves between the mid-1980s and 1995–1997. Two changes have occurred in the intervening period that could affect Se cycling in the Bay. First, beginning in the mid-1980s, an invading species of bivalve, *Potamocorbula amurensis*, became the predominant benthic macroinvertebrate in the Bay (Carlton et al., 1990). Biological invasions of estuaries have become an increasing problem worldwide and are known to change community structure and function (Cohen and Carlton, 1998; Carlton and Geller, 1993). *P. amurensis* is a voracious feeder that has essentially eliminated the standing stock of phytoplankton from the water column of the Suisun Bay (Cloern, 1996). The result has been an increase in energy available to the benthic food web and a decrease in energy available to the water column food web (J. Thompson, USGS, personal communication). Second, greater than normal precipitation and high river runoff occurred during this study period (May 1995–November 1997), in contrast to the periods of drought that characterized earlier study periods. This could result in more selenium



Selenium Sample Locations

Fig. 1. Shoal (S) and Channel (C) sites sampled in North San Francisco Bay for *P. amurensis* in May 1995, October 1995 and October 1996.

entering the Bay from the agricultural runoff than occurred previously. Our study investigates several questions:

- have selenium concentrations in the predominant benthos changed after the invasion of *P. amurensis*?
- Are the seasonal and spatial patterns of selenium contamination different from those recorded earlier?
- Is selenium contamination focused in specific habitats where the element might be expected to accumulate (shallow waters vs. adjacency to marshes vs. deeper channel waters)?
- Is selenium uptake by *P. amurensis* different than in co-occurring species or experimentally transplanted species?

## 2. Experimental design

Four experiments were conducted to evaluate the implications of the invasion and the status of selenium contamination. To establish a reliable baseline of Se concentrations in the bivalves and evaluate seasonal variability, samples were collected near monthly from October 1995 through November 1997 at the station nearest Carquinez Strait (USGS 8.1), traditionally the most Se-contaminated reach of the Bay-Delta. Additional sites were added to resolve the spatial distribution of selenium enrichment in the bivalves. In October 1995, *P. amurensis* were collected from five locations in the tidal reaches of the Napa River and one site toward the river mouths from Carquinez Strait (USGS 6.1). The Napa River meets the Bay at Carquinez Strait, where Se concentrations have been highest. In October it is expected that the Napa River and the Bay exchange water in both directions throughout the sampling area (D. Schoelhammer, USGS, personal communication). Twenty-four sites were sampled in October 1996 to compare contamination in San Pablo and Suisun Bays and to compare deeper water sites (four stations) to shallow sites (20 stations) adjacent to different marshes. Finally, to evaluate if transplanted bivalves yielded results typical of the native community, *P. amurensis* were collected in May 1995, October 1995 and October 1996 from

three sites near those used in bivalve transplants by the San Francisco Bay Regional Monitoring Program (RMP; Fig. 1). These sites were in Grizzly Bay, Carquinez Strait (USGS 8.1) and San Pablo Bay-Pinole Point (USGS 12.5).

## 3. Methods

Resident clams (*P. amurensis*) were collected from the subtidal zone with a Van Veen grab and 1 or 2 mm sieves. Channel depths ranged from 8 to 20 m. The subtidal sites adjacent to marshes in Honker Bay and the Napa River (Fig. 1) were located in the shallows at an average depth of 1–3 m. Clams were also collected intertidally at low tide with a shovel, sieve and bucket. Between 60 and 120 clams of all sizes were collected at each time and each site and placed into containers of water collected at the site. The clams were kept in this ambient water in a constant temperature room at 10 °C to depurate for 48 h, as previous studies showed a residence time of material in the gut of *P. amurensis* to be approximately 24 h (Decho and Luoma, 1991). Clams from each site were separated into size classes of 1 mm difference and similar sized individuals were composited. Samples of larger numbers of individuals were necessary for smaller size classes in order to obtain enough mass for analysis. Soft tissues were dissected from the shell and tissues. Each composite was then lyophilized and homogenized. Mean concentrations characteristic of a site at a particular time were determined from analyses of three replicate composite samples each containing 20–60 individuals (each composite contained at least 250 mg dry weight (dw) soft tissue).

Selenium in the bivalves was determined by hydride atomic absorption spectrophotometry. Selenium subsamples were digested in concentrated nitric and perchloric acids at 200 °C, reconstituted in hydrochloric acid, and then stored until analysis. All glassware and field collection apparatus were acid washed, thoroughly rinsed in ultra-clean deionized water, dried in a dust-free positive pressure environment, sealed and stored in a dust free cabinet. Quality control was maintained by frequent analysis of blanks, analysis of

National Institute of Standards and Technology standard reference materials (tissues and sediments) with each analytical run, and internal comparisons with prepared quality control standards. Analyses of National Institute of Technical Standards (NITS) reference materials (oyster tissue, San Joaquin soils) were within an acceptable range of certified values reported by NITS (data in Luoma and Linville, 1996).

Water and particulate samples were collected in June 1995 and October 1996 using methodologies described earlier (Cutter, 1989). Pre-cleaned teflon Go-Flo sampling bottles were used to obtain water 1 m below the surface. The water was filtered through pre-cleaned and pre-weighed 0.45  $\mu\text{m}$  Nucleopore membrane filters into 1 l linear polyethylene bottles and acidified to pH 1.5 with HCl. Filters were carefully folded, placed in polyethylene vials and immediately frozen. Total dissolved selenium was determined by boiling a 4 M HCl acidified sample with potassium persulfate solution for 1 h; then analyzing as a selenite sample by selective generation of hydrogen selenide, liquid nitrogen-cooled trapping, and atomic absorption detection (0.01  $\text{mol l}^{-1}$  detection limit). The standard additions method of calibration was used to ensure accuracy and all determinations were made in triplicate. Particulate selenium determinations were made using digestion procedures described by Cutter (1985) and procedures for reducing iron concentrations described by Cutter (1989). Filters were dried at 40  $^{\circ}\text{C}$ , re-weighed, then digested using a three step nitric-perchloric acid digestion. After iron removal by passage through an anion exchange resin, the digest was analyzed as a total selenium sample.

## 4. Results and discussion

### 4.1. River discharge

River discharges could influence allochthonous inputs of selenium from the San Joaquin River. Probably more important are the inflows from the Sacramento River, which has very low selenium concentrations and dilutes enriched Se inputs to

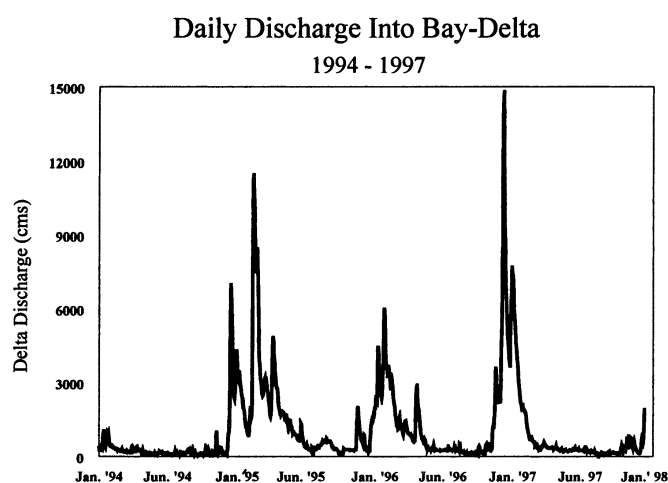


Fig. 2. Daily river discharge into San Francisco Bay, determined as net delta outflow at Chipps Island in Suisun Bay, between 1 January 1994 and 30 November 1997, as  $\text{m}^3 \text{s}^{-1}$ .

the Bay (Cutter, 1989). The Mediterranean climate of the area drives a seasonal cycle in river discharge and causes large year-to-year variability in discharge. Nearly all precipitation occurs in the watershed between approximately November and April. The early flow is trapped in dams and snowfall; the highest river flows typically occur from January through approximately June, followed by low river flows through the rest of the year (Fig. 2). Interannual differences also reflect differences in precipitation. The period of record for the present study, 1995–1997, was characterized by high peak river inflows and, especially in 1995, a prolonged period of elevated river discharge. Previous studies of selenium in San Francisco Bay occurred between 1976 and 1977 and 1986 and 1990. Both were periods of prolonged drought, except for a flood in April 1986. Fig. 2 contrasts the patterns of river discharge in 1995–1997 to a typical drought year (1994) when both the magnitude and the period of high river discharges are reduced (also see hydrograph in Johns et al., 1988).

### 4.2. Selenium in the water column

Fig. 3(a) compares total dissolved selenium concentrations in estuarine transects from June 1995 to October 1996, with concentrations determined by the same methods in September 1986

(Cutter, 1989). All values are plotted as a function of salinity. Arrows depict the location of Carquinez Strait in each transect. Selenium concentrations in the Bay in 1995–1996 exceeded those in the Sacramento River, as in previous studies ( $0.065 \pm 0.022 \mu\text{g Se per l}$ ; Cutter and San Diego-McGlone, 1990). The highest concentration in the Bay was  $0.29 \mu\text{g l}^{-1}$ . Within the Bay-Delta the concentrations at most stations followed the order June 1995 < October 1996 < September 1986, but the differences among the three transects were small, and appear to fall with the range of variation defined by Cutter and San Diego-McGlone (1990). The shape of the October 1996 transect differed from that in September 1986 because of elevated selenium concentrations at the upstream-most station, perhaps indicating some San Joaquin input. Total dissolved Se concentrations

were low compared with the USEPA water quality standard of  $5 \mu\text{g Se per l}$  (Environmental Protection Agency, 1992).

Particulate selenium is the variable most likely to ultimately determine selenium bioavailability (Luoma et al., 1992). Concentrations of selenium on suspended particulate material were determined only in October 1996, during the present study. Particulate selenium was uniformly higher in Oct 1996 than in the estuarine transect conducted in September 1986 (Cutter, 1989; Fig. 3(b)). The highest concentration was observed in the river station in October 1996 (nearly  $8 \mu\text{g g}^{-1}$  dw), again indicating particulate selenium inputs from the San Joaquin River were possible (subsequent studies have not found these high values, however; Cutter et al., unpublished data).

#### 4.3. Selenium in *P. amurensis*

##### 4.3.1. Spatial variability

Among the stations that were sampled in May 1995, selenium concentrations in soft tissues of *P. amurensis* ranged from  $3.7 \pm 0.7$  to  $7.1 \pm 0.3 \mu\text{g Se per g dw}$  (Table 1). Se concentrations were higher in *P. amurensis* from the Carquinez Strait ( $7.1 \mu\text{g Se per g dw}$ ), than ( $P < 0.01$ ) in the shallows of Suisun Bay ( $3.9 \mu\text{g Se per g dw}$ ) and San Pablo Bay ( $3.7 \mu\text{g Se per g dw}$ ). The latter two sites were not statistically different. Concentrations in October 1995 were higher than in May 1995. Se in *P. amurensis* from Carquinez Strait ( $15.4 \mu\text{g Se per g dw}$ ) and Suisun Bay ( $14.5 \mu\text{g Se per g dw}$ ) were not statistically different; but both were higher than Se concentrations in San Pablo Bay ( $11.6 \mu\text{g Se per g dw}$ ;  $P < 0.05$ ; Table 1). Concentrations were also elevated in the tidal Napa River compared with May concentrations in the North Bay.

Concentrations of Se in *P. amurensis* in October 1996 were similar to October 1995 (Table 1; Fig. 4). The range of mean Se concentrations in *P. amurensis* was  $6.9$ – $8.7 \mu\text{g Se per g dw}$  in San Pablo Bay, and  $5.9$ – $20 \mu\text{g Se per g dw}$  in Suisun Bay. The greatest enrichment was observed in the Carquinez Strait ( $20.0 \mu\text{g Se per g dw}$ ). Higher concentrations were observed toward the rivers, at stations S1–S6, compared with other shallow water locations in Suisun Bay or San Pablo Bay

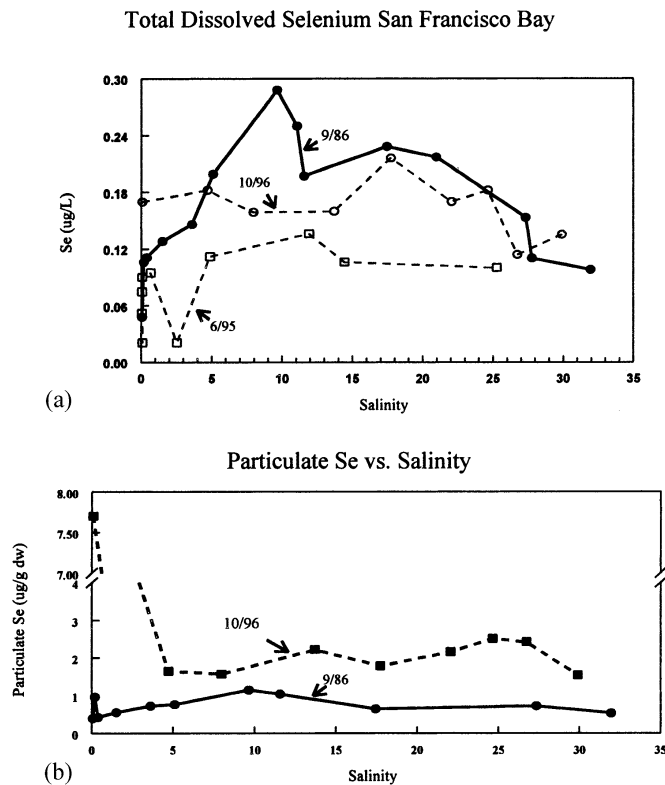


Fig. 3. (a) Dissolved Se concentrations ( $\mu\text{g Se per l}$ ) as a function of salinity, determined in transects across the salinity gradient of North San Francisco Bay in September 1986 (Cutter, 1989), June 1995 and October 1996. (b) Concentrations of particulate Se ( $\mu\text{g Se per g dw}$ ) as a function of salinity determined in transects across the salinity gradient of North San Francisco Bay in September 1986 (Cutter, 1989) and October 1996.

Table 1

Selenium concentrations in  $\mu\text{g g}^{-1}$  dw in *P. amurensis* at 29 locations in North San Francisco Bay (Fig. 1) in May 1995, October 1995, and October 1996

Site	Se ( $\mu\text{g g}^{-1}$ dry)	Standard deviation (S.D.)	Sample composites
<i>May 1995</i>			
Grizzly Bay	3.9	0.8	5
8.1 (Carq. Straits)	3.7	0.7	3
San Pablo Bay-Pinole Pt.	7.1	0.3	3
<i>October 1995</i>			
6.1	14.5	1.4	3
8.1 (Carq. Straits)	15.4	1.0	3
12.5 (San Pablo)	11.6	1.1	5
Napa 1	12.5	1.0	3
Napa 2	15.3	n/a	1
Napa 3	14.1	0.5	3
Napa 4	14.0	0.9	3
Napa 5	12.7	0.7	2
Napa 6	12.6	0.8	5
<i>October 1996</i>			
4.1	11.0	1.0	7
6.1	16.8	1.6	5
8.1 (Carq. Straits)	20.0	1.4	4
12.5 (San Pablo)	8.7	2.1	4
S1	9.6	0.2	2
S2	9.2	0.1	2
S3	7.5	0.1	2
S4	10.0	0.0	2
S5	8.9	0.4	5
S6	10.3	0.8	2
S7	5.9	1.6	4
S8	6.1	0.3	2
S9	8.2	0.7	4
S10	6.7	0.2	3
S11	7.3	0.3	4
S12	8.3	0.3	2
S13	8.1	0.5	2
S14	8.1	0.7	3
S15	6.9	1.2	3
S16	7.5	0.3	3
S17	7.9	0.7	2

Each sample composite included approximately 20–60 individual *P. amurensis*, and >250 mg dw soft tissue. Napa River stations are numbered North-to-South ascending. Stations S1–S17 are in shallow water.

( $P < 0.001$ ; Table 1; Fig. 4). Like dissolved and particulate concentrations in October 1996, the higher concentrations toward the rivers in *P. amurensis* could have reflected inputs from the San Joaquin River.

Thus all three samplings of bivalves indicate that Se concentrations in *P. amurensis* are enriched compared with background concentrations

typical of bivalves ( $< 3 \mu\text{g Se per g}$ ; Johns et al., 1988) and that enrichment is widespread through North San Francisco Bay. Concentrations varied nearly 4-fold among sites. The observation of the highest concentrations near Carquinez Strait is consistent with past studies (Cutter, 1989; Johns et al., 1988) and the previously identified refinery source of Se input. Dilution of contamination (i.e.

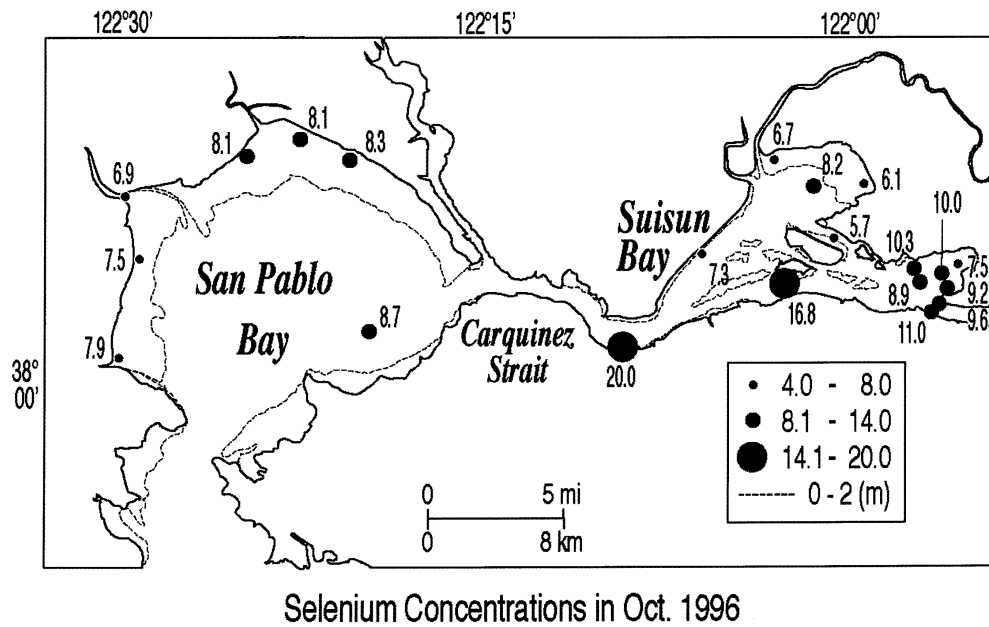


Fig. 4. Map showing distribution of mean Se concentrations in *P. amurensis* ( $\mu\text{g Se per g dw}$ ) at 20 locations in Suisun and San Pablo Bays, in North San Francisco Bay, in October 1996. Standard deviations (S.D.) are shown in Table 1. Site codes are shown in Fig. 1.

the lowest concentrations in *P. amurensis*) near the eastward marshes in Suisun Bay and the western-most shallows of San Pablo Bay are consistent with dilution away from the refineries. Sources and mixing appeared to be more important than shallow versus deep-water habitat, despite the possibility that selenium is trapped in shallow wetlands. Some riverine input is also possible. Long residence times and complicated, tidally driven circulation patterns (Burau et al., in prep.) probably contribute to the somewhat complicated pattern of the contamination in *P. amurensis* in Suisun and San Pablo Bay during periods of low river inflow.

#### 4.4. Temporal variability

Selenium concentrations in *P. amurensis* from Carquinez St. varied as much as three-fold seasonally between May 1995 and November 1997 (Fig. 5). The lowest concentrations were observed in May 1995 ( $7.1 \pm 0.3 \mu\text{g Se per g dw}$ ) and May 1997 ( $6.2 \pm 0.2 \mu\text{g Se per g dw}$ ). Concentrations were highest in October 1995 to February 1996 ( $15.4 \pm 1.0 \mu\text{g g}^{-1}$ – $18.9 \pm 0.4 \mu\text{g Se per g dw}$ ), October 1996 ( $20 \pm 1.4 \mu\text{g Se per g dw}$ ), and

November 1997 ( $15.3 \pm 3.4 \mu\text{g Se per g dw}$ ). The larger standard deviations in the four samples in late 1997 are probably the result of employing fewer individual animals per composite.

The seasonal pattern of selenium in *P. amurensis* from Carquinez Strait coincided with seasonal changes in river inflows. The lowest concentrations always occurred after episodes of highest river inflows and shortest hydraulic residence

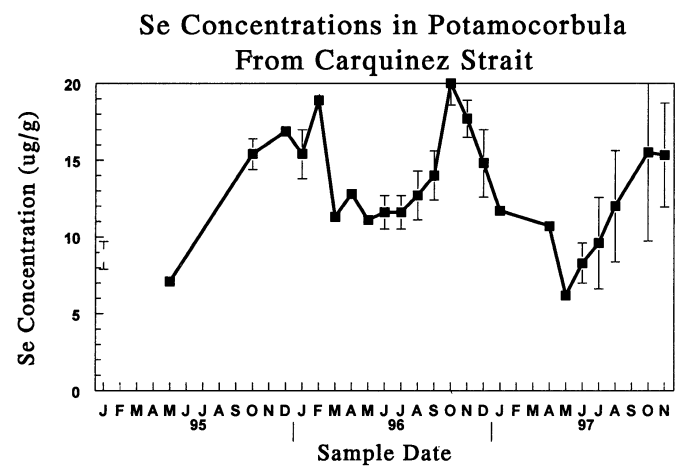


Fig. 5. Mean and S.D. of Se concentrations in *P. amurensis* ( $\mu\text{g Se per g dw}$ ) at site C8.1 as determined at near monthly intervals between May 1995 and November 1997.



times. The greatest increase in Se occurred after prolonged periods of low flow, as hydraulic residence times increased. Increased Se bioaccumulation with increased residence times has been reported in other systems (Lemly, 1998). In contrast, Johns et al. (1988) did not observe strong seasonality in concentrations of Se in *Corbicula fluminea* in Suisun Bay, in the mid-1980s. One important difference was that that study did not include periods of river inflows as high or as prolonged as those occurring in 1995–1997.

#### 4.5. Comparison to historic concentrations in bivalves

The selenium concentrations in *P. amurensis* in Suisun and San Pablo Bay are considerably higher than found in bivalves, in general, in uncontaminated estuaries in Northern California (1.7–3.1  $\mu\text{g}$  Se per g dw, Johns et al., 1988; White et al., 1988). Data from *P. amurensis* itself is not available from uncontaminated estuaries. Concentrations in *P. amurensis* are also higher than in earlier studies from the Bay. Selenium exposures in the bivalves *Mytilus edulis* and *C. fluminea* were studied near Carquinez Strait in 1975 and 1984–1986, respectively (Risebrough, 1977; Johns et al., 1988). Risebrough et al. (1977) reported a mean concentration of  $8 \pm 3$   $\mu\text{g}$  Se per g dw in transplanted *M. edulis* from four sites near Carquinez Strait and concentrations of 10–11.4  $\mu\text{g}$  Se per g dw in bivalves deployed directly in Carquinez Strait. These were some of the highest concentrations in the Bay at that time. Johns et al. (1988) sampled resident *Corbicula amurensis* at near monthly intervals from a station toward the rivers from Carquinez Strait (the most seaward population of *Corbicula* present in Suisun Bay at the time). In 67 samples they found a mean concentration of  $6 \pm 3$   $\mu\text{g}$  Se per g dw in the clams. Mean selenium concentrations in *P. amurensis* among all the samples reported above ( $15 \pm 3$   $\mu\text{g}$  Se per g dw) were higher than found previously in either *M. edulis* or *C. fluminea*. The dominant bivalve in Suisun Bay changed from *C. fluminea* in 1985–86 to *P. amurensis* after the invasion of the latter species (Carlton et al., 1990; Nichols et al., 1990), so an increase in the exposure of ben-

thic predators to Se is likely if they consumed the invasive bivalve.

#### 4.6. Comparison to monitoring with co-occurring and transplanted bivalves

Some species possess characteristics that enhance their bioaccumulation of contaminants. High assimilation efficiencies of selenium are typical of most marine organisms (Reinfelder et al., 1997; Wang and Fisher, 1999). But some species (copepods are an example) lose selenium rapidly ( $\sim 0.15$  per day) compared with other elements (Wang and Fisher, 1998), whereas loss rates from bivalves are slow (0.01–0.03 per day; Luoma et al., 1992; Reinfelder et al., 1997). Efficient assimilation and slow loss means that bivalves have generally strong capabilities to bioaccumulate selenium in their tissues (Reinfelder et al., 1997). *P. amurensis* is an unusually voracious filter feeder, it has an unusually short gut residence time (Decho and Luoma, 1991) and it utilizes a variety of food sources. All of these traits could enhance its ability to bioaccumulate Se, even compared with other bivalves.

Direct comparisons with co-occurring species are difficult with *P. amurensis*, because it tends to replace other bivalves and consumer organisms (Nichols et al., 1990). In June 1997 we found *P. amurensis* from a Carquinez Strait mudflat had  $12.9 \pm 1.2$   $\mu\text{g}$  Se per g dw and a co-occurring population of *M. balthica* contained  $3.7 \pm 0.1$   $\mu\text{g}$  Se per g dw. But this was only one coincident sampling. A comparison of *P. amurensis* with *C. fluminea* toward the rivers in Suisun Bay found similar concentrations in both species in October 1996, but sample sizes were very small. Conclusive determination of any special bioaccumulative characteristics of *P. amurensis* await further comparisons with co-occurring species and comparative kinetic studies.

An alternative approach is to compare Se bioaccumulation in *P. amurensis* with values in transplanted bivalves used to monitor the Bay. In the RMP of the San Francisco Estuarine Institute (SFEI, 1995, 1996), bivalves are transplanted for 90–100 days then contaminant uptake is compared with concentrations observed before the

Table 2

Comparison of selenium concentrations in transplant and resident species in North Bay in May 1995, October 1995 and October 1996

Site	Species transplant	Change in condition index ( $T_F - T_o$ )	Se ( $\mu\text{g g}^{-1}$ dry) [ $T_F - T_o$ ]	Species: resident	Se ( $\mu\text{g g}^{-1}$ dry)
<i>May 1995</i>					
Grizzly Bay	<i>C. fluminea</i>	0.018	1.4 [−0.3]	<i>P. amurensis</i>	$3.9 \pm 0.8$
Napa R. (Carquinez)	<i>C. gigas</i>	−0.022	6.2 [4.6]	<i>P. amurensis</i>	$7.1 \pm 0.3$
San Pablo Bay-Pinole Pt.	<i>C. gigas</i>	0.006	5.4 [3.8]	<i>P. amurensis</i>	$3.7 \pm 0.7$
<i>October 1995</i>					
Grizzly Bay	<i>C. fluminea</i>	−0.02	4.8 [0.1]	<i>P. amurensis</i>	$14.5 \pm 1.4$
Napa R. (Carquinez)	<i>C. gigas</i>	−1.04	2.9 [−0.2]	<i>P. amurensis</i>	$15.4 \pm 1.0$
San Pablo Bay-Pinole Pt.	<i>M. californianus</i>	−0.02	2.5 [−0.8]	<i>P. amurensis</i>	$11.6 \pm 1.1$
<i>October 1996</i>					
Grizzly Bay	<i>C. fluminea</i>	−0.038	2.9 [1.3]	<i>P. amurensis</i>	$8.2 \pm 0.7$
Napa R. (Carquinez)	<i>C. gigas</i>	−0.089	7.2 [2.9]	<i>P. amurensis</i>	$20 \pm 1.4$
San Pablo Bay-Pinole Pt.	<i>M. californianus</i>	−0.039	2.7 [−2.4]	<i>P. amurensis</i>	$8.7 \pm 2.1$

For transplanted species the final concentration is presented with the level of bioaccumulation of selenium over deployment period ( $T_F - T_o$ ) displayed in brackets. The change in condition index over the period of deployment, a measure of growth (or lack of feeding), is also presented. 'Transplant' data from SFEI, 1995, 1996.

deployment. The RMP employs three different bivalves, due to differing salinities in the Bay, *C. fluminea* is used in Suisun Bay; the oyster *Crassostrea gigas* is used near Carquinez Strait; and the mussel *Mytilus californianus* is used in San Pablo Bay. Three of the sampling locations used for *P. amurensis* were near the above locations used by the RMP, and the 1995–1996 studies with *P. amurensis* were conducted at the same time as an RMP sampling.

Table 2 shows concentrations of Se in the transplants and the level of bioaccumulation, or lack thereof, during deployment in May 1995, October 1995 and October 1996. Changes in condition index over the deployment period are also shown; and these are compared with concentrations in the resident *P. amurensis* at the end of the deployment period of the transplanted species. Absolute concentrations of Se in tissues and patterns of bioaccumulation in time and space are compared. The differences in absolute concentrations were small in May 1995. But substantial differences were

observed between the deployed bivalves and *P. amurensis* in both October 1995 and October 1996. In October 1995, selenium concentrations in *P. amurensis* were 11.6–15.4  $\mu\text{g Se per g dw}$  among the three sites. None of the deployed species bioaccumulated Se during the deployment (concentrations were similar to the original population) and concentrations ranged from only 2.5 to 4.8  $\mu\text{g Se per g dw}$  (Table 2). A similar result occurred in October 1996. In that experiment, bioaccumulation of selenium was observed in *C. gigas* but concentrations were less than half those in *P. amurensis* at a nearby site. No significant bioaccumulation occurred in *C. fluminea*, although the concentration of Se in *P. amurensis* at that site was  $8.2 \pm 0.7 \mu\text{g Se per g dw}$ . Thus the seasonal pattern of greatly increased bioaccumulation in October compared with May was clear in *P. amurensis* but was not observed in the deployed animals.

The approach used to study bioaccumulation may be the cause of the differences between Se

bioaccumulation in *P. amurensis* and the transplants, *C. fluminea*, *C. gigas* or *M. californianus*. Phytoplankton blooms in Suisun Bay have essentially disappeared since the *P. amurensis* invasion, presumably due to consumption of primary production by the invasive bivalve. It is notable that condition index appeared to decline in all transplants in both October experiments (Table 2). Reduced condition index after deployment suggests that the deployed bivalves were not feeding normally in the fall. Uptake from food is the predominant route of selenium exposure (Luoma et al., 1992; Wang and Fisher, 1999). Therefore, it is possible that non-feeding deployed animals were not exposed to environmental selenium. The deployed animals gave no indication that high selenium concentrations were common in the predominant benthic species in North Bay during the season of low river inflows. Thus, the transplanted animals did not provide an accurate picture of selenium contamination in the estuary, and did not reach the level of selenium contamination found in *P. amurensis*.

#### 4.7. Consequences of high selenium concentrations in *P. amurensis*

Bivalves are a critical link for passing selenium to benthivores because trophic transfer is the primary route of predator exposure (Lemly, 1985). The highest concentrations of Se in *P. amurensis* are especially significant in that they exceed values that other studies have shown reduce growth or cause reproductive damage when ingested in experiments by birds and fish (Hamilton et al., 1990; Heinz et al., 1989). Teratogenicity, effects on hatchability of eggs and reduced growth of young life stages have a threshold of occurrence above 3–10  $\mu\text{g Se per g dw}$  in food in various studies (Lemly, 1998; Hamilton, 1999; Heinz et al., 1989). A high frequency of adverse effects is found when concentrations in food (prey) exceed 10–11  $\mu\text{g Se per g dw}$  (Skorupa, 1998; Adams et al., 1998). The highest concentrations in *P. amurensis* exceed the latter value by two-fold.

Some of the important resource species in the North Bay/Delta eat *P. amurensis* and presumably other bivalves (sturgeon, diving ducks

such as scoter and scaup, dungeness crab; Carlton et al., 1990). Earlier studies (White et al., 1988; Urquhart and Regalado, 1991) showed that these benthivores were the predators with the highest selenium concentrations. Average yearly Se concentrations in the liver of the diving duck, surf scoter, ranged from 75 to 200  $\mu\text{g g}^{-1} \text{ dw}$  in 1986–1990, a 7- and 14-fold increase from a reference site (Humboldt Bay). White sturgeon captured between 1986 and 1990 contained annual average concentrations ranging from about 9–30  $\mu\text{g Se per g dw}$  in liver ( $n = 52$ ); and 7–15  $\mu\text{g Se per g dw}$  in flesh ( $n = 99$ ). In 1986, the Dungeness crab had an average soft tissue concentration of 15  $\mu\text{g Se per g dw}$ , which was a three fold increase from the reference site (Humboldt Bay). Predators that fed from the water column (e.g. striped bass) seemed to have lower selenium concentrations than the benthivores.

If the susceptibility of San Francisco Bay to invasion by the exotic species *P. amurensis* (Carlton et al., 1990) caused greater Se contamination in the benthos, this effect could be passed on to benthivores. Little data is available to evaluate selenium concentrations in benthivores after 1990. But the 5-year Se Verification Study extended from 1986 through 1990 (Urquhart and Regalado, 1991). *P. amurensis* was first observed in the Bay in 1986 and became well established by 1988 (Carlton et al., 1990; Nichols et al., 1990). Annual mean selenium concentrations in bivalves and two benthivores, sturgeon and scoter, were collected simultaneously in that study and in several of the years between 1986 and 1990. Bivalve selenium concentrations (not including *P. amurensis*) and benthivore concentrations were strongly correlated in that data set (Figs. 6 and 7). The highest values in benthivores were observed in 1989 and 1990. If the mean concentration of selenium in *P. amurensis* was inserted into Fig. 7 at the 1989–1990 benthivore concentration, the added point is consistent with changing selenium exposures of predators. Thus preliminary analysis indicates that the successful invasion of this new resident of Suisun Bay could have changed the exposure of at least some predators in this system.

## 5. Conclusions

Invasion of San Francisco Bay by the exotic bivalve, *P. amurensis*, resulted in an increase by threefold of selenium concentrations in the predominant macrobenthic food in the estuary. Se concentrations in bivalve-consuming benthivores in the North Bay appeared to increase between the time *P. amurensis* populations were first observed (1986, Carlton et al., 1990) and when it became established as the predominant benthic species (~1988–1990; Urquhart and Regalado, 1991). This is of concern because Se is a strong reproductive toxin for such species, and Se concentrations in *P. amurensis* in fall 1995 and 1996 were in excess of the toxicologic threshold for adverse effects on such predators. Se-contaminated *P. amurensis* were widespread in Suisun and San Pablo Bays in 1995 and 1996. Seasonal variability is an important feature of selenium contamination in *P. amurensis*, with the highest concentrations occurring in fall during the period of longest hydraulic residence times. Transplanted bivalves were not good surrogate indicators for exposure and contamination of the resident bivalve.

### Selenium in Benthos Carquinez Strait

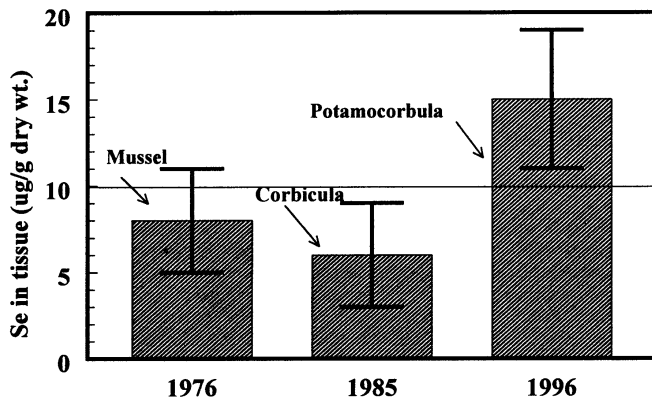
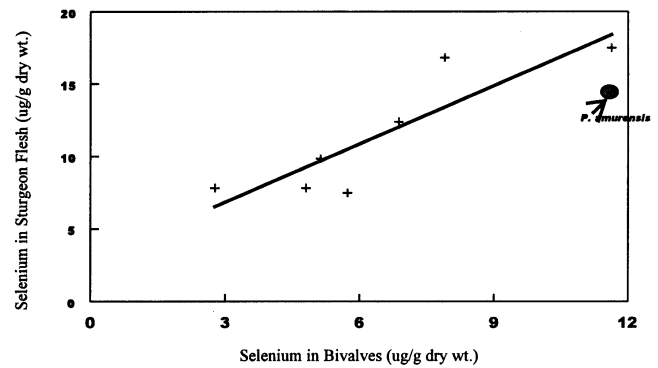


Fig. 6. Mean and S.D. of Se concentrations ( $\mu\text{g Se per g dw}$ ) in three studies of bivalves from in or near Carquinez Strait in three different decades. 'Mussels' were studies of transplanted *M. edulis* in 1976 (Risebrough et al., 1977); 'Corbicula' represents mean of 67 samplings of the clam *C. fluminea* (Johns et al., 1988) and 'Potamocorbula' is the mean of all Carquinez samples in the present study.

### Bivalves v. Sturgeon Flesh



### Bivalves v. Scoter Flesh

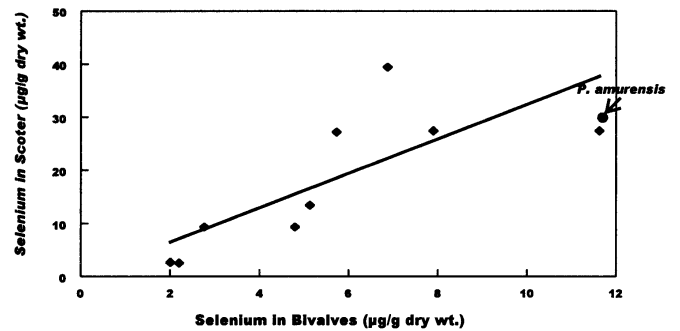


Fig. 7. Relationships between Se concentrations in resident bivalves (data from White et al., 1988; Urquhart and Regalado, 1991; Johns et al., 1988) and either sturgeon flesh or the flesh of the diving ducks (surf scoter) from North San Francisco Bay and Humboldt Bay (data from White et al., 1987, 1988, 1989; Urquhart and Regalado, 1991). Predators and prey were sampled in the same season, year and sub-bay. Mean Se concentration in *P. amurensis* at Carquinez in 1995 is superimposed on each graph to match predator data from 1989–1990, because *P. amurensis* was probably the primary food of these predators in 1989–1990.

We did not fully disprove the hypothesis that the invasive species, *P. amurensis*, is not more efficient at bioaccumulating selenium than other bivalves, although some evidence points in that direction. But this is not the only way an invasive species can affect the fate and effects of a contaminant. The efficient bioaccumulation of Se by bivalves, in general, and the efficient dietary transfer of Se from bivalves to higher trophic levels means that an invasion that shifts the structure of an estuarine community toward dominance by a bivalve-based benthic food web can enhance adverse effects of selenium in the system, by expand-

ing the availability of a contaminated food supply. Whatever the basic mechanism, it seems clear that the invasion of the non-native bivalve *P. amurensis* has resulted in increased bioavailability of a potent environmental toxin to certain benthivores in San Francisco Bay. Changes in contaminant cycling and potential effects are yet another reason to be concerned by the threat of invasive species in our estuarine ecosystems (Cohen and Carlton, 1998; Carlton and Geller, 1993).

### Acknowledgement

Selenium analyses of *P. amurensis*, and quality control of those samples, were from the laboratory of A. Horowitz and K. Ehrlick, U.S. Geological Survey.

### References

- Adams, W.J., Brix, K.V., Cothorn, K.A., Tear, L.M., Cardwell, R.D., Fairbrother, A., Toll, J.E., 1998. Assessment of selenium food chain transfer and critical exposure factors for avian wildlife species: need for site-specific data. In: Little, E.E., DeLonay, A.J., Greenberg, B.M. (Eds.), Environmental Toxicology and Risk Assessment: Seventh Volume. ASTM STP, p. 1333.
- Brown, C.L., Luoma, S.N., 1995. Use of the euryhaline bivalve *Potamocorbula amurensis* as a biosentinel species to assess trace metal contamination in San Francisco Bay. Mar. Ecol. Prog. Ser. 124, 129–142.
- Carlton, J.T., Geller, J.B., 1993. Ecological roulette—the global transport of nonindigenous marine organisms. Science 261, 78–82.
- Carlton, J.T., Thompson, J.K., Schemel, L.E., Nichols, F.H., 1990. The remarkable invasion of San Francisco Bay (California, USA) by the Asian clam *Potamocorbula amurensis*. I. Introduction and dispersal. Marine Ecol. Prog. Ser. 66, 81–94.
- Cloern, J.E., 1996. Phytoplankton bloom dynamics in coastal ecosystems: a review with some general lessons from sustained investigation of San Francisco Bay, California. Rev. Geophy. 34, 127–168.
- Cohen, A.N., Carlton, J.T., 1998. Accelerating invasion rate in a highly invaded estuary. Science 279, 555–558.
- Cutter, G.A., 1985. Determination of selenium speciation in biogenic particles and sediments. Anal. Chem. 57, 2951–2955.
- Cutter, G.A., 1989. The estuarine behaviour of selenium in San Francisco Bay: Estuarine. Coastal Shelf Sci. 28, 13–34.
- Cutter, G.A., Bruland, K.W., 1984. The marine biogeochemistry of selenium: a reevaluation. Limnol. Oceanogr. 29, 1179–1192.
- Cutter, G.A., San Diego-McGlone, M.L.C., 1990. Temporal variability of selenium fluxes in San Francisco Bay. Sci. Total Environ. 97/98, 235–250.
- Decho, A.W., Luoma, S.N., 1991. Time-courses in the retention of food material in the bivalves *Potamocorbula amurensis* and *Macoma balthica*: significance to the absorption of carbon and chromium. Mar. Ecol. Prog. Ser. 78, 303–314.
- Diplock, A.L., 1976. Metabolic Aspects of Selenium Action and Toxicity, CRC Critical Reviews in Toxicology.
- US Environmental Protection Agency, 1992. Rulemaking: water quality standards: establishment of numeric criteria for priority toxic pollutants: States' compliance: Final Rule. 57 Fed. Reg. 60848, 22 December 1992. Washington, DC.
- Hamilton, S.J., 1999. Hypothesis of historical effects from selenium on endangered fish in the Colorado River Basin. Hum. Ecol. Risk Assess. 5, 1153–1180.
- Heinz, G.H., Hoffman, D.J., Gold, L.G., 1989. Impaired reproduction of mallards fed an organic form of selenium. J. Wildl. Manage. 53, 418–428.
- Hodson, P.V., Hilton, J.W., 1983. The nutritional requirements and toxicity to fish of dietary and waterborne selenium. Ecology. Bull. 35, 335–340.
- Johns, C., Luoma, S.N., Eldrod, V., 1988. Selenium accumulation in benthic bivalves and fine sediments of San Francisco Bay, the Sacramento-San Joaquin Delta and selected tributaries. Estuarine Coastal Shelf Sci. 27, 381–396.
- Largier, J.L., 1996. Hydrodynamic exchange between San Francisco Bay and the ocean: The role of ocean circulation and stratification. In: Hollibaugh, J.T., (Ed.) San Francisco Bay The Ecosystem: Further Investigations into the Natural History of San Francisco Bay and Delta With Reference to the Influence of Man.
- Lemly, A.D., 1985. Toxicology of selenium in a freshwater reservoir: implications for environmental hazard evaluations and safety. Ecotoxicol. Environ. Safety 10, 314–338.
- Lemly, A.D., 1995. A protocol for aquatic hazard assessment of selenium. Ecotoxicol. Environ. Safety 34, 223–227.
- Lemly, A.D., 1998. Pathology of selenium poisoning. In: Frankenberger, W., Engberg, R.A. (Eds.), Environmental Chemistry of Selenium. Marcel Dekker, New York, pp. 315–354 (pp. 281–296).
- Luoma, S.N., Linville, R.G., 1996. A comparison of selenium and mercury concentrations in transplanted and resident bivalves from North San Francisco Bay. Annual Report of Regional Monitoring Program, 1995. San Francisco Estuary Institute, pp. 160–171.
- Luoma, S.N., Johns, C., Fisher, N., Steinberg, N.A., Oremland, R.S., Reinfelder, J.R., 1992. Determination of selenium bioavailability to a benthic bivalve from particulate and solute pathways. Environ. Sci. Tech. 26, 485–491.
- Monismith, S.G., Burau, J.R., Stacey, M., 1996. Stratification dynamics and gravitational circulation in northern San Francisco Bay. In: Hollibaugh, J.T., (Ed.) San Francisco

- Bay The Ecosystem: Further Investigations into the Natural History of San Francisco Bay and Delta With Reference to the Influence of Man.
- Nichols, F.H., Cloern, J.E., Luoma, S.N., Peterson, D.H., 1986. The modification of an estuary. *Science* 231, 567–573.
- Oremland, R.S., Steinberg, N.A., Maest, A.S., Miller, L.G., Hollibaugh, J.T., 1990. Measurement of in situ rates of selenate removal by dissimilatory bacterial reduction in sediments. *Environ. Sci. Technol.* 24, 1157–1164.
- Phillips, D.J.H., Rainbow, P.S., 1993. *Biomonitoring of Trace Aquatic Contaminants*. Elsevier, London, p. 371.
- Presser, T.S., Ohlendorf, H.M., 1987. *Biogeochemical Cycling of Selenium in the San Joaquin Valley*, vol. 11. Environmental Management, California, USA, pp. 805–821.
- Reinfelder, J.R., Wang, W.X., Luoma, S.N., Fisher, N.S., 1997. Assimilation efficiencies and turnover rates of trace elements in marine bivalves: a comparison of oysters, clams and mussels. *Marine Biol.* 129, 443–452.
- Risebrough, R.W., Chapman, J.W., Okazaki, R.K., Schmidt, T.T., 1977. *Toxicants in San Francisco Bay and Estuary*. Report to the Association of Bay Area Governments, Berkeley, CA, pp. 38.
- SFEI, 1995, 1995. *The Regional Monitoring Program for Trace Substances*. San Francisco Estuary Inst, Richmond, CA, p. 385.
- SFEI, 1996, 1996. *The Regional Monitoring Program for Trace Substances*. San Francisco Estuary Inst, Richmond, CA, p. 360.
- Skorupa, J.P., 1998. Selenium poisoning of fish and wildlife in nature: lessons from twelve real-world examples. In: Frankenberger, W., Engberg, R.A. (Eds.), *Environmental Chemistry of Selenium*. Marcel Dekker, New York, pp. 315–354.
- Stadtman, T.C., 1974. Selenium biochemistry. *Science* 183 (128), 1915–1922.
- Urquhart, K.A.F., Regalado, K., 1991. *Selenium Verification Study, 1988–1990*. Water Resources Control Board Rept. 91 -2-WQ, Sacramento, CA, pp. 176.
- Wang, W.-X., Fisher, N.S., 1998. Accumulation of trace elements in a marine copepod. *Limnol. Oceanograph.* 43, 273–283.
- Wang, W.-X., Fisher, N.S., 1999. Delineating metal accumulation pathways for marine invertebrates. *Sci. Total Environ.* 237/238, 459–472.
- White, J.R., Hofmann, P.S., Hammond, D., Baumgartner, S., 1987. *Selenium Verification Study, 1986*. Water Resources Control Board Rept., Sacramento, CA, pp. 79.
- White, J.R., Hofmann, P.S., Hammond, D., Baumgartner, S., 1988. *Selenium Verification Study, 1986–1987*. Water Resources Control Board Rept., Sacramento, CA, pp. 60.
- White, J.R., Hofmann, P.S., Urquhart, K.A.F., Hammond, D., Baumgartner, S., 1989. *Selenium Verification Study, 1987–1988*. Water Resources Control Board Rept., Sacramento, CA, pp. 81.
- Wrench, J.J., 1978. Selenium metabolism in the marine phytoplankters *Tetraselmis tetrathele* and *Dunaliella minuta*. *Mar. Biol.* 49, 231–236.
- Wrench, J.J., Measures, C.I., 1982. Temporal variations in dissolved selenium in a coastal ecosystem. *Nature* 299, 431–433.