Lessons Learned About Metals in the Estuary:

The Importance of Long-term Clam Accumulation Data

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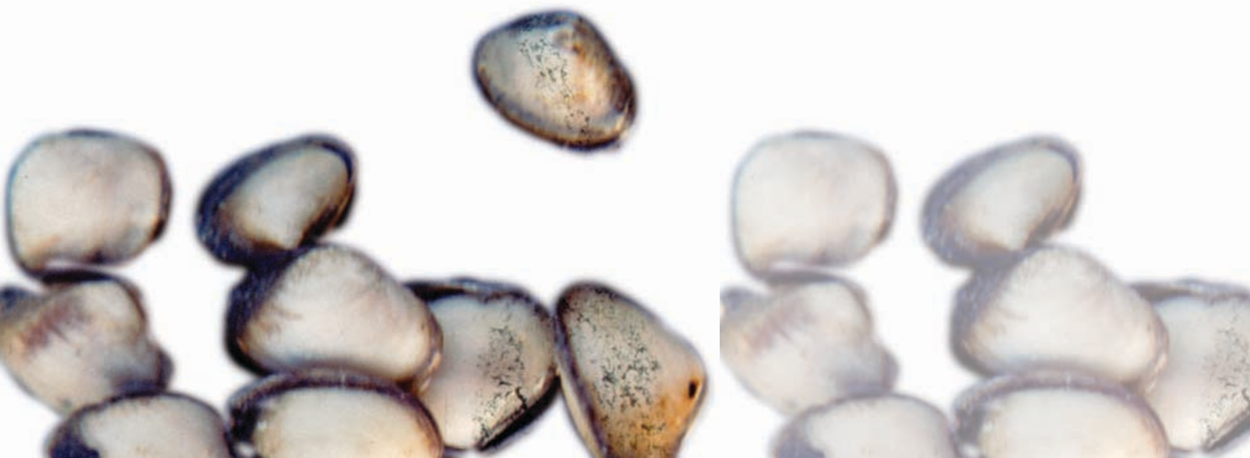
Key Points

- ***Natural variability can create difficulty in understanding processes in a complex estuary such as San Francisco Bay, it can also provide opportunities to examine the factors that regulate accumulation of metals in estuarine species***
- ***Freshwater inflow is a primary influence on accumulation of some metals***
- ***Silver concentrations have declined significantly in the South Bay, with the greatest declines occurring in the 1980s, before the RMP began its sampling***
- ***Evidence strongly points to silver (perhaps in combination with copper) as a potential disrupter of clam reproduction at concentrations well below those typically used in toxicity tests***



Introduction

Trace metals can be an influential factor in ecosystem processes, affecting the well-being of organisms, populations, and communities (Luoma 1996). Metal bioaccumulation in tissues of clams and other bottom dwelling organisms is an indicator of metal exposures that can either degrade the health of the organism, or be transferred up the food web to potentially harm higher organisms. It is critical to understand the interaction between ecosystem processes and the bioaccumulation of metals to begin to evaluate the metals' importance in the ecosystem.

Ecosystems are complex and variable. Environmental factors such as hydrology, water chemistry, sediment characteristics, and food availability fluctuate widely from year-to-year in estuaries and affect interpretation of pollutant influences. Yet on the time scale of a decade or more, consistent increases or decreases over time in the environmental factors are rare. If effects of pollutant exposure are imposed on this system, they cannot be separated, convincingly, in a few years of sampling. However, if pollutant inputs are declining over time, as has happened often in the United States since the passage of the Clean Water Act in 1972, the downward trend in exposure may be the only long-term trend in the data. So even though variability can create difficulty in understanding processes in a complex estuary such as San Francisco Bay, it can also provide opportunities to examine the factors that influence accumulation of metals in estuarine species. This article describes work performed under the US Geological Survey Toxic Substances Hydrology Program, which is unique among estuarine studies in its long-term approach to quantitatively defining the processes that affect contaminant transport and distribution in major urbanized estuaries (Kuwabara et al. 1999).

Background of work

Bioaccumulation in the clams *Potamocorbula amurensis* and *Macoma balthica* has been used to assess both the fate and effects of trace metals in San Francisco Bay (Brown and Luoma 1995, Brown et al. 2003, Linville et al. 2002). By comparing this high-intensity, long-term data set with other long-term environmental data sets (e.g., river inflow, amount of suspended sediments in the water column, salinity, and reproduction in the clams), various processes affecting the availability of metals to the biota in the ecosystem have been examined. Four challenges to understanding trace metal bioavailability and effects illustrated by the data are discussed here:

1) do river inflows affect the bioavailability of different metals?

2) what is the influence of water chemistry (salinity)?

3) can metal effects be separated from other influences in an environment this complex? and

4) how does history affect interpretations of long-term data sets?

Freshwater inflow is a primary influence on metal accumulation

The northern portion of San Francisco Bay is influenced by large seasonal and year-to-year fluctuations in freshwater inflow from the Sacramento and San Joaquin rivers, which combine to provide 90% of the freshwater inflow into the Bay (Conomos et al. 1985). Each year is characterized by a distinct high and low inflow period driven by the Mediterranean climate of the region, snowmelt runoff, and controlled releases from the reservoirs. River inflow is highest in the winter/spring and lowest in the summer/fall. The magnitudes of these fluctuations differ among years. A major challenge in ascertaining the fate and effects of metals is understanding the influences of this highly variable flow regime.

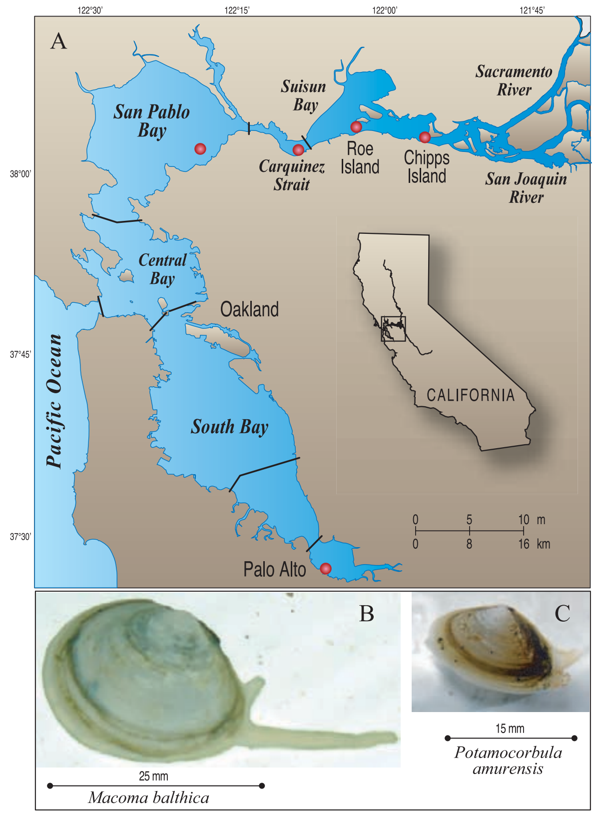


Figure 1. San Francisco Bay is a complex and variable ecosystem. A) Map of San Francisco Bay with four sites in the northern reach of the Bay (Chipps Island, Roe Island, Carquinez Strait, and San Pablo Bay) and one site (Palo Alto) in the southern portion. B) *Macoma balthica*, the deposit feeding clam collected in the mudflat at the Palo Alto site. C) *Potamocorbula amurensis*, the suspension feeding clam collected in the channel at the northern reach sites.

Our sampling occurred over a period of extreme year-to-year differences in weather and inflow. Drought conditions occurred in 1989 through 1992, and 1994, when the annual mean inflow of freshwater from the rivers was 152 - 252 cubic meters per second ($m^3\ s^{-1}$). The wet season of 1993 marked the end of a seven-year drought with annual mean inflow of 760 $m^3\ s^{-1}$. Annual mean inflow increased to a range of 1094 - 1823 $m^3\ s^{-1}$ in 1995-1999 (Interagency Ecological Program [IEP] 2002). The seasonal and yearly variability in freshwater flow exposed the species living in this segment of San Francisco Bay to changes in salinity, river-borne contaminant inputs, carbon load, and distribution of sediments and contaminants. Although inflows were highly variable from year-to-year, there was no overall trend in the variability over the 10-year study period.

The two time scales of change in inflows are examples of predictable and unpredictable variability. The extreme year-to-year differences are not predictable in advance. But, the seasonal pattern in variability of river inflow, and the environmental factors related to river inflow, is somewhat predictable. A relatively predictable spatial (landward-to-seaward) gradient in salinity also reflects the seasonal influences. In sampling over a long time period, the differences between years can be viewed as “natural experiments” that provide insights into seasonal processes. But interpreting the outcome of those experiments requires a sampling strategy that captures seasonal variability, so differences among years can be separated from variability within years. Understanding the patterns in both year-to-year and seasonal variability is critical to understanding the differences between natural and anthropogenic effects on the ecosystem.

Metal Abbreviations

Ag (silver)

Cd (cadmium)

Cr (chromium)

Cu (copper)

Hg (mercury)

Ni (nickel)

Pb (lead)

V (vanadium)

Zn (zinc)

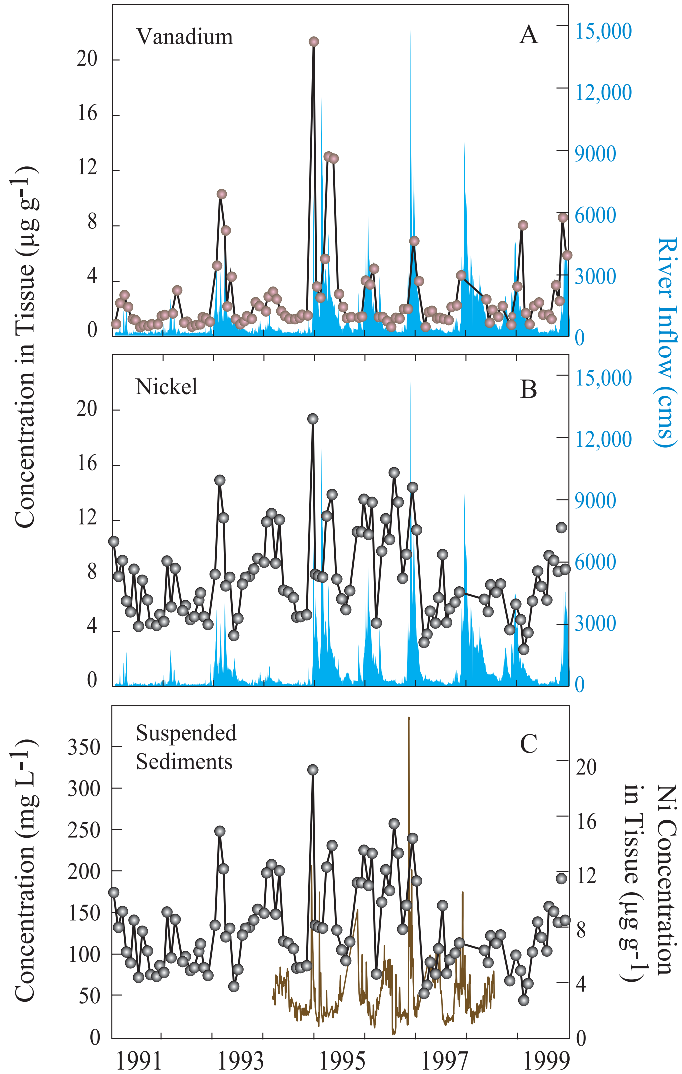


Figure 2. The seasonal patterns of vanadium and nickel in clam tissue suggest both are brought into the Bay by inflow from the Sacramento/San Joaquin rivers. In contrast, nickel also has sources within the Estuary. A) Monthly mean tissue concentrations of V in *Potamocorbula amurensis* at Carquinez Strait over the length of the study (1991-1999) compared with river inflow. Vanadium tissue concentration increased in clams only when river inflow was high during wet winter months. These data indicate that the primary source of V to the Estuary is from the rivers. B) Monthly mean tissue concentrations of Ni ($\mu g\ g^{-1}$) in *Potamocorbula* at Carquinez Strait over the length of the study (1991-1999) compared with river inflow. Nickel tissue concentrations increased in clams when river inflow was high in the wet winter months, but also increased again in the dry windy summer months. C) Monthly mean tissue concentrations of Ni ($\mu g\ g^{-1}$) in *Potamocorbula* at Carquinez Strait over the length of the study (1991-1999) compared with near-bottom suspended-solid concentration data showed evidence of Ni sources within the Bay, in particular wind/wave resuspension of bottom sediments, causing an increase in the accumulation of Ni.

Within the tissues of *Potamocorbula*, river inflow variability is the primary influence on the accumulation of the metals chromium (Cr), nickel (Ni), and vanadium (V). These metals are important because they are common in the Estuary and are environmental contaminants. They are enriched in certain rocks that are common throughout the watershed and thus are naturally high in the sediments in the Bay. Vertical cores of sediments indicate that the high concentrations of Cr, Ni, and V extend back to before the Gold Rush and the acceleration of human activities in the area (Hornberger et al. 1999). Each also has industrial sources in the northern reach of San Francisco Bay such as oil refining, chemical manufacturing, mining activities, and steel refining. Specific forms of V, Cr, and Ni that commonly occur in aquatic environments are known to be toxic, but little is known about their bioavailability in estuaries, especially regarding V.

The seasonal pattern of Cr, Ni, and V concentrations in the tissues of the clams suggests that freshwater flow into the Bay from the Delta affects their bioaccumulation. Vanadium has the strongest relationship with river inflow (Figure 2a). Vanadium concentrations increase during pulses of high inflows and are low in the tissues at all stations during low flow periods. Tissue concentrations at the most landward site, near Chipps Island, are often as low as tissue concentrations at

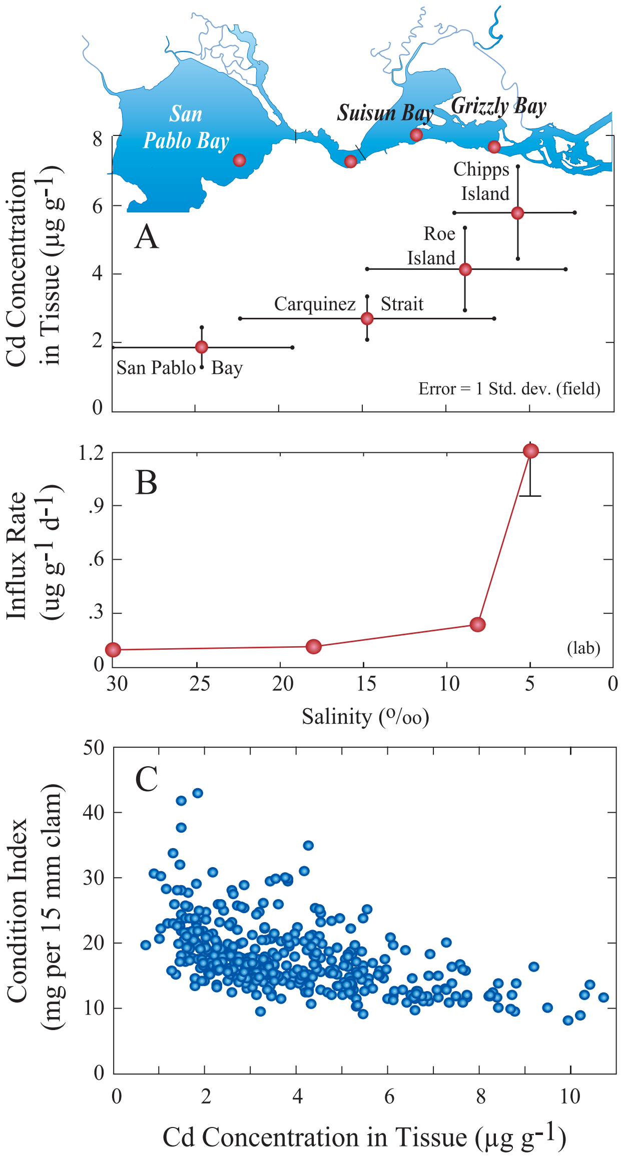


Figure 3. Salinity can also influence the bioaccumulation of contaminants. Cadmium in the tissues of *Potamocorbula amurensis* and its relationship to the salinity gradient in the northern reach of San Francisco Bay shows the influence of salinity on bioaccumulation.
A) Cadmium (µg g^{-1}) in the tissues of *Potamocorbula* at each station over the entire period of the study compared with salinity at each station. Cadmium was more readily accumulated by the clams at lower salinities.
B) Laboratory experiments confirmed that Cd at low salinities was more readily accumulated by the clam. Uptake of Cd by the clam increased as salinity decreased. This information reinforced field observations. C) Cadmium may have affected the health of the clam, as seen in this comparison with the condition index. The range of condition is greatest in clams with low Cd tissue concentrations. As Cd concentrations in the clam increased, the clams were less able to gain weight and lose weight in their normal life cycle.

the most seaward site, San Pablo Bay, during low flows. However, when river inflows increase, concentrations of V are higher in clams at Chipps Island than in clams in San Pablo Bay.

Nickel (Figure 2b) and Cr (not shown) tissue concentrations behave similarly to V during high flows. But during low flow periods, tissue concentrations of Ni (and Cr) do not decrease to the lowest levels seen in San Pablo Bay, and the land-to-sea gradient is sustained (Figure 2b). Potential input of Ni from internal industrial or sedimentary sources could explain an apparent Ni source within the Estuary that appears to add to the Ni from the watershed; the influence of these internal sources is most evident when freshwater inflows decrease (less Ni input from the watershed) (Topping and Kuwabara, 2003). Measurement of near-bottom suspended solids concentrations (SSC, the amount of sediment suspended in the water column) was used to evaluate whether resuspension of Ni and Cr trapped in the bottom sediments, during the windy summer months, might prevent summer concentrations in the clams from dropping to low values (Buchanan and Ruhl, 2001, Figure 2c). Annually, the pattern of SSC followed a pattern similar to river inflow, with highest concentrations of SSC coinciding with highest river inflow within each year. The first annual increase in SSC coincided with river inflow and peaked to the highest concentrations of the year (200-400 mg L^{-1}). These peaks were fairly short in duration (2-3 months), and then SSC decreased to concentrations representing the lowest of the year (10-20 mg L^{-1}). However, following the first peak and drop in SSC, a second rise in SSC occurred during the dry summer months (low flow period). It was not as high as the first peak of the year (75-100 mg L^{-1}), and was of longer duration (4-5 months). This second rise in SSC was similar from year-to-year in magnitude and duration and occurred when wind velocity was the greatest and resuspension of bottom sediments was dominant throughout the Bay. As mentioned above regarding river inflow, V tissue concentrations dropped to annual lows (and Bay-wide lows) at each station during the low flow periods. Vanadium tissue concentrations never increased during the second SSC rise that occurred each year during the dry summer months. In contrast to V, the seasonal pattern of Ni tissue concentrations more closely followed that of the SSC seasonal pattern. Ni concentrations peaked during the high river inflow peak, dropped to lowest annual concentrations (at each station) following that peak, and then increased again coincident with the second, longer SSC peak. This pattern was observed at every station.

The trends for Cr, Ni, and V in the tissues of *Potamocorbula* show how physical processes and natural sources within an ecosystem interact with anthropogenic inputs to affect metal bioaccumulation. Bioaccumulation of these three metals appears to be primarily controlled by the interaction of the hydrodynamics and natural sources in the watershed, with secondary influences by anthropogenic (industrial discharge) and natural processes (sediment resuspension) within the northern reach of San Francisco Bay.

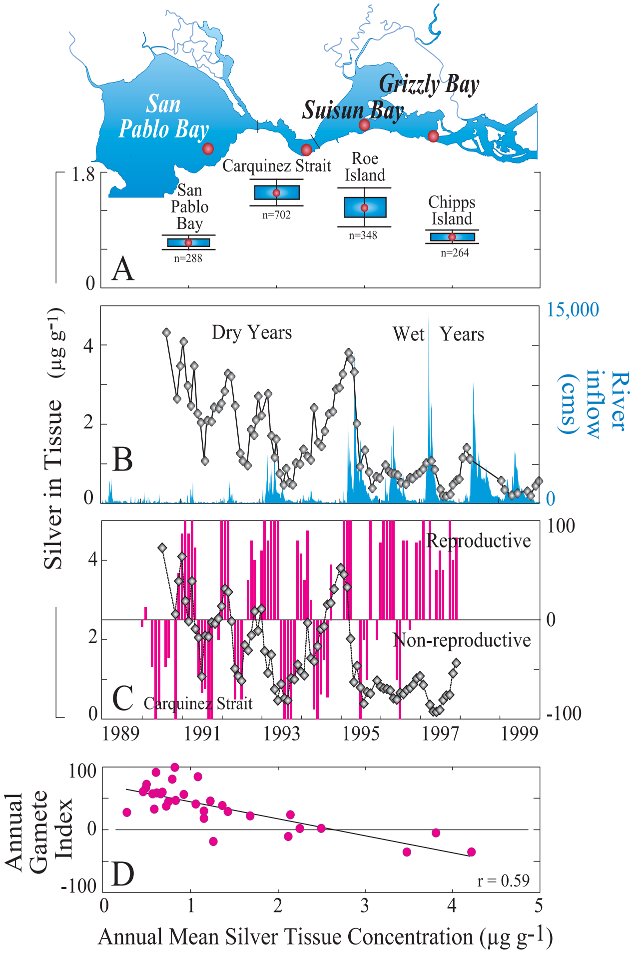


Figure 4. Long term monitoring in clams provided evidence of a detrimental effect of silver on clam reproduction. A) Grand mean silver tissue concentrations in *Potamocorbula* at each site in the northern portion of San Francisco Bay. The points represent the grand means of all data from 1990-1999 in µg g^{-1} dry weight, with number of samples (n) per mean shown at the bottom of each box plot. The boxes represent 1 standard error and the whiskers represent 1.96 standard error. Silver concentrations in *Potamocorbula* were highest at the two mid-estuary sites (Roe Island and Carquinez Strait) and lowest at the two end-estuary sites (San Pablo Bay and Chipps Island) suggesting a mid-estuary source. B) Monthly mean silver concentrations (µg g^{-1} dry weight, left axis) in the tissues of *Potamocorbula* at Carquinez Strait plotted with the river hydrograph (m^3 s^{-1}, right axis). The bioaccumulation of silver by *Potamocorbula* was linked to the timing and length of high inflow periods of freshwater from the Sacramento and San Joaquin rivers into the northern portion of San Francisco Bay. C) Monthly mean silver concentrations (µg g^{-1} dry weight, right axis) in the tissues of *Potamocorbula* at Carquinez Strait plotted with the central tendency of the reproductively active and non-reproductively active *Potamocorbula* (left axis) at each site. Central tendency of the reproduction data is the proportion of clams that were reproductively active (% active + % ripe + % spawned) minus the proportion of clams that were non-reproductively active (% inactive + % spent) collected each month. The timing of the increase in proportion of reproductively active clams coincided with the timing of the decrease of silver in the tissues of *Potamocorbula*. D) Correlation between the annual proportions (%) of reproductive clams (*Potamocorbula*) with the annual mean silver concentrations (µg g^{-1} dry weight) at the four sites. Y-axis represents the central tendency of the reproduction data. Net reproductively active populations are positive (plot above the zero line) and net non-reproductively active populations are negative (plot below the zero line). Populations with high silver in their tissues have a significantly lower proportion of reproductive clams.

Water chemistry (salinity) affects cadmium bioaccumulation

A second challenge to understanding bioaccumulation of trace metals in San Francisco Bay is variable water chemistry (salinity). A good example is cadmium (Cd) concentrations in *Potamocorbula amurensis* (Figure 3). There is not the distinct flow-related seasonal trend in the Cd tissue concentrations that is seen in Cr, Ni, and V. However, there is a seasonally consistent spatial pattern (Figure 3a). Cadmium concentrations are highest in clams near Chipps Island and lowest in clams in San Pablo Bay. This pattern is consistent among all the years of the study. Potential sources of cadmium include oceanic upwelling, urban and industrial effluents, and mining. It is not clear which source is dominant for the clams, because both geochemical processes and anthropogenic inputs could contribute. Dissolved cadmium concentrations in the Sacramento and San Joaquin Rivers are lower than dissolved concentrations in the Pacific Ocean (SFEI 2003). However, Cd is more available to the biota from fresh water. Cadmium dissolved in river water is mostly in a form highly accessible to clams (the free ion). When the river water mixes with the ocean water, Cd forms chloro-complexes that are less available to the clams than the free ion. The spatial gradient of Cd in the clams is correlated to the salinity gradient, consistent with this switch in chemical form. Cadmium in the clams nearest the rivers (Chipps Island, lower salinity) is consistently higher than Cd in the clams closer to the ocean (San Pablo Bay, higher salinity).

The effect of salinity on Cd uptake was studied with *P. amurensis* in the laboratory. This work confirms that Cd at low salinities is more available to the clam. There was an increase in Cd uptake by the clam as salinity decreased (Figure 3b). The critical salinity where uptake greatly increased was less than 6 PSU. These results reinforced what was observed with the field data.

Long-term data sets allow for the integration of environmental data with trace metal data to further the understanding of processes in this complicated ecosystem

An indicator of the overall fitness of *Potamocorbula* measured coincident with the metal data showed significant correlations with the cadmium tissue concentrations (Figure 3c). Condition index values followed a pattern that was the inverse of the Cd tissue concentrations. Clams have their lowest condition index near Chipps Island where Cd tissue concentrations are highest and their highest condition index in San Pablo Bay where Cd tissue concentrations are lowest. The details of this relationship between Cd and condition index are not clear and have not been fully examined.

Detecting metal impacts in a complex estuary

A third challenge in understanding processes that influence bioaccumulation of trace metals in San Francisco Bay is detecting the effects of sources within the Bay in such a complex environment. The example is silver (Ag) and *Potamocorbula* (Figure 4; Brown et al. 2003). Silver is an element of importance in aquatic systems because it is highly toxic and readily accumulated through the combination of its reactivity with chlorides in seawater and the ease with which it becomes bound by suspended sediment particles (in contrast to Cd, the chloride complexation of silver in estuaries makes it available to organisms; Luoma et al. 1995). Silver occurs in such low concentrations naturally that its presence in moderate to high concentrations is almost always indicative of an anthropogenic source.

The spatial distribution of Ag in *Potamocorbula* indicated that a site-specific source occurred in the middle region of the study area (Figure 4a). On all time scales (monthly, annual means, or means for the decade), the highest Ag tissue concentrations in *Potamocorbula* occurred at the two mid-estuary sites, Roe Island and Carquinez Strait. When data from all 10 years were aggregated, concentrations at Roe Island and Carquinez Strait were significantly higher (two-fold) than the two end-estuary sites at Chipps Island and San Pablo Bay. The central estuarine peak made detection of impacts easier, because there is not a co-variance with factors like salinity or carbon/organic matter input from river flows.

Changes through time in Ag accumulation were partly driven by the hydrology of the Estuary. The variability of silver concentrations was related to the pattern of freshwater inflow from the Sacramento and San Joaquin rivers (Figure 4b); most noticeably at the site of highest silver concentrations (Carquinez Strait). However, the influence of river inflow on Ag accumulation was opposite from what was observed with Cr, Ni, and V. For example, in most years, Ag concentrations in the clams at Carquinez Strait decreased as high (winter) river inflow began. During the period of low river inflow, concentrations in the tissues steadily increased until the next episode of high river inflow began. Deviations from this pattern occurred at Carquinez Strait only in very low flow years. For example, in 1993, tissue Ag concentrations declined after the winter rains, but steadily increased through 1994 (a critically dry year), to levels as high as those seen in 1990. After 1995, there were no periods of low flow that extended beyond the typical seasonal pattern, and Ag in the tissues did not accumulate as high as they had prior to 1995. This suggested that the longer the period of low flow, the greater the accumulation of Ag.

Silver in the tissues of the clam showed a similar negative relationship with condition index as seen with cadmium. In addition, differences in silver accumulation in the tissues also correlated with changes in the reproductive activity of the clam (Figure 4c). This was not observed for Cd. Clams were collected for reproduction analysis concurrently with the clams collected for metal analyses. Gender and developmental stage of the gonads were characterized in at least 10 specimens at each time and place. Five qualitative stages of gonad development were described: inactive, active, ripe, spawning, and spent. Clams in the active, ripe and spawning stages were defined, for simplicity, as reproductively active. Clams in the inactive and spent stages were considered non-reproductive. Data for reproduction were available through 1997 (Parchaso and Thompson 2002).

Reproductive activity decreased whenever tissue concentrations of silver increased above 1 - 2μg/g Ag in the clam tissues (Figure 4c). Monthly sampling was essential for identifying the reproductive status of the different populations because of the complex annual pattern of the maturation of gonadal tissues. Each population of clams from the four sites showed a different reproductive pattern over the length of the study. At Carquinez Strait (Figure 4c), a majority of clams were reproductive in 61% of the months sampled through 1997. During the period of highest Ag contamination (Figure 4b), up until 1995 at Carquinez Strait, many months occurred when most clams were non-reproductive (Figure 4c). When Ag concentrations in the tissues were highest (annual mean > 1 µg g^{-1}), the clams were reproductively active only 20†– 60% of the year. Prior to 1995, the pattern of reproductive activity at this mid-Estuary site was different than landward at Chipps Island or seaward at the San Pablo Bay site (low Ag tissue concentrations). The proportion of reproductively mature clams at these sites averaged 80 – 100% through all years. As Ag concentrations declined, the proportion of months the clams were reproductively mature at Carquinez Strait increased to values similar to those at the Chipps Island and San Pablo Bay sites (after 1995), and remained at 80-100% for the duration of the study. Across all times and places (Figure 4d), when Ag concentrations in the tissues of the clams were at an annual mean < 1µg g^{-1}, the clams were reproductively active 80-100% of the year. A significant negative correlation between annual mean Ag tissue concentrations and reproductive activity was observed (Figure 4d).

Absent any additional data, the relationship between Ag in *Potamocorbula* tissues and reduced reproductive activity alone would not be sufficient to indicate causality. But the intense spatial and temporal sampling allowed demonstration of: 1) coincidental changes in both time and space; 2) lack of co-variance with aspects of the estuarine gradient that could cause stress (salinity) or affect food availability (freshwater input); 3) a rigorous representation of the entire reproductive cycle, so correlations were not happenstance. Brown et al (2003) discussed the necessary criteria to draw a strong association between exposure and effects in a field study and concluded that the Ag and reproductive effects in *P. amurensis* met those criteria.

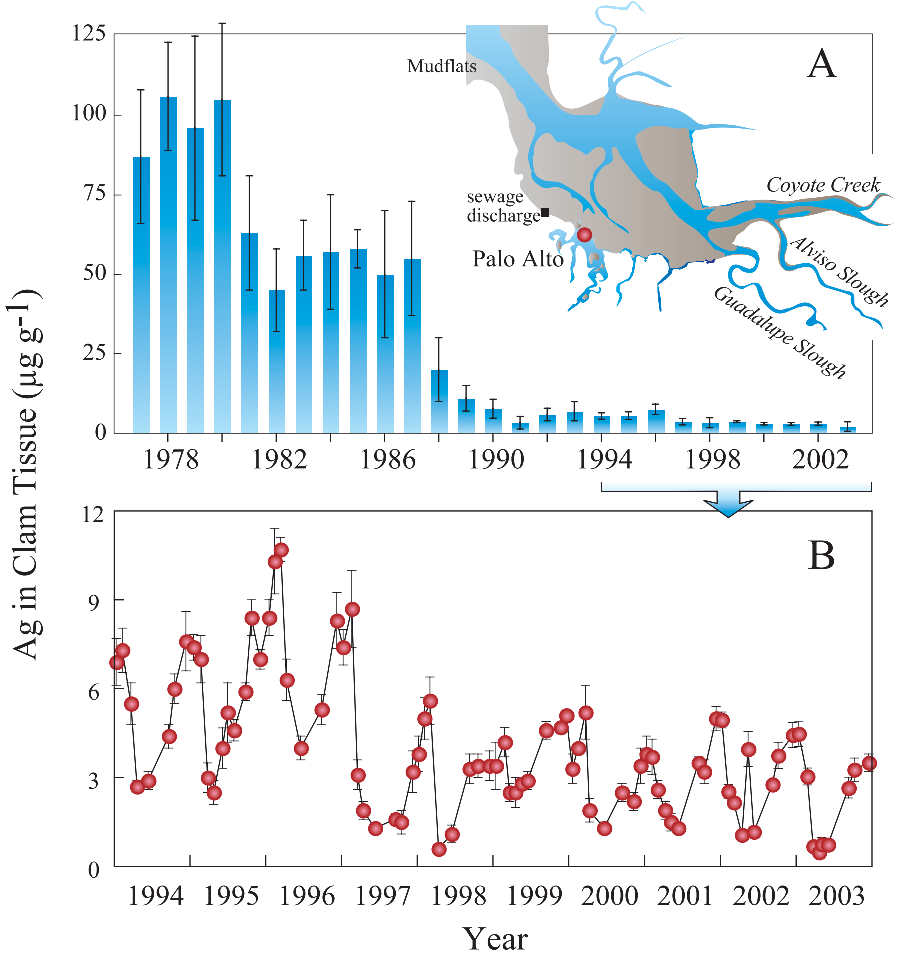


Figure 5. Annual trends of silver in *Macoma balthica* from the Palo Alto site in the southern reach of San Francisco Bay show the importance of a long term perspective when assessing progress in Estuary clean-up. A) Annual average trend of declining Ag tissue concentrations (µg g^{-1}) between 1977 and 2003. The decline in silver was unambiguous until 1990. B) After 1990, silver in the clams fluctuated in concentration from year-to-year, with some additional decline in recent years.

The importance of a long term perspective

The association observed in northern San Francisco Bay between Ag exposure as indicated by tissue concentration and changes in reproductive activity in *Potamocorbula* was also observed at a site in the southern portion of San Francisco Bay (Hornberger et al. 2000) (Figure 1a). The South Bay study generated another long time-series (1977-1999), but using a different clam species, *Macoma balthica* (Figure 1b) as a bioindicator. Metals were determined in *Macoma* and sediments at an intertidal mudflat, one kilometer south of the Palo Alto Water Quality Control Plant. Before 1990 only Cu, Ag and Zn were determined. After 1990, the data include a larger suite of metals and metalloids (Luoma et al., 1998). Like the North Bay situation, this facility had reported high concentrations of silver in their effluent.

Trends in metal concentrations in sediments varied. Concentrations of Cd, Cr, Hg, Pb, Se, and V in the 1970s and 1980s were similar to concentrations typical of the Bay region in the 1990s (Hornberger et al. 1999). In contrast, Cu and Ag concentrations declined between 1975 and 1998. Average silver concentrations in surface sediments decreased by 87% from 1.6 µg g^{-1} in 1977 to 0.2 µg g^{-1} in 1991 (the year of lowest concentration). Average concentrations of

Cu in surface sediment decreased by 50% from 86 μg g^{-1} in 1979 to 43 μg g^{-1} in the year of lowest concentration, 1993.

Concentrations of both Ag and Cu in *Macoma* were extremely high in the late 1970s, compared to those typically found worldwide in this type of bioindicator (e.g. Luoma and Phillips 1980). Because the seasonality in Cu and Ag concentrations was characterized by the near monthly sampling, unbiased comparisons of annual mean concentrations were possible. The annual average trend of declining Ag (and Cu, not shown) concentrations between 1977 and 1990 was unambiguous (Figure 5a). Studies elsewhere in South Bay support the possibility that a Bay-wide decline in Ag concentrations has occurred in that region since the 1970s (Stephenson and Leonard 1994). After 1990, both metals fluctuated in concentration from year-to-year, with some additional decline in Ag concentrations in recent years (Figure 5b).

During the course of the study, general environmental conditions varied widely, but did not progressively change. A variety of wet and dry years occurred, including El Niño events and periods of drought. Monthly salinity varied from 5 to 33 over the >20 year study period and followed seasonal and year-to-year rainfall patterns. Sediment characteristics, like particle size and total organic carbon, varied seasonally and year-to-year, but did not change progressively (Thompson-Becker and Luoma 1985). Phytoplankton productivity may influence food availability for clams in South San Francisco Bay (Nichols and Thompson 1985); but like other variables, the magnitude and frequency of phytoplankton blooms varied from year-to-year and showed no progressive trends. Thus, factors that might influence metal bioaccumulation or clam reproduction, such as food availability, redox, particle size, salinity, temperature, isolation, or hydrodynamics were not related to the progressive change in metal exposures of the clams, nor were any of the factors progressively different for the period for which reproductive data were available. The decline in concentrations of Cu in *Macoma* between 1977 and 1988 was strongly correlated to declining metal concentrations and loads from the Palo Alto treatment plant.

Hornberger et al. (2000) showed the improvement in reproductive capabilities in *Macoma* after Ag and Cu concentrations declined. Mature gonadal tissues were not observed, during any month of the year, in more than 50% of individual clams when the concentrations of Ag and Cu were elevated. The evidence indicated *Macoma* was probably not reproducing successfully at Palo Alto in most years before 1989. After contamination receded in 1989, mature gonadal tissues returned. These observations suggest chemical disruption of reproduction by Ag and/or Cu. Other environmental factors show no such association and thus are unlikely causes. Other signs of stress in *Macoma* during the period of high metal exposure supported the suggestion of chemical disruption.

One unique aspect of the Palo Alto data set is that it began before widespread monitoring was common in the Bay. The greatest declines in contamination occurred in the 1980s, before the RMP began its sampling. From RMP data alone, one might conclude that efforts to improve waste treatment in the South Bay have had little impact. But when a more robust history of South Bay is considered, it is clear that great changes happened before 1990 in response to investments in waste treatment facilities. Since the 1990s, regional processes (perhaps recycling of contamination from sediments; or inputs from urban runoff) have been more important factors in controlling contamination than improvements in any single waste treatment facility.

The remarkable consistency in biological response in two independent and separate episodes (seen in *Potamocorbula* in the North Bay and *Macoma* in the South Bay) also strongly points to Ag (perhaps in combination with Cu) as potential disrupters of reproduction in clams at concentrations well below those typically used in toxicity tests. Most natural confounding factors (food, salinity, temperature) were eliminated as possible causative agents of the reproductive effects in both cases. A lack of information on organic contaminants prevents them from being discounted as possible stressors, but patterns of the effects in space and time were not consistent with what is known about these contaminants.

Conclusions

The data presented here show that bioaccumulation and the impacts of one contaminant do not necessarily explain the patterns of bioaccumulation of other contaminants. Environmental processes affect the availability of metals in different ways. Each of the metals discussed showed different accumulation patterns, which in turn facilitated the determination of the different processes involved in creating these patterns. As compellingly shown with Ag, inputs of trace metals can cause adverse biological effects that are detected in the Estuary. Changes in flow conditions may be very important for the availability of metals to the system. For example, if flow is limited, silver is more bioavailable, so hydrology may indirectly cause impairment of reproductive processes.

Only such a long-term data set allows for the integration of hydrodynamics, sediment dynamics, reproduction, and biogeochemistry data along with the trace metal data to further the understanding of processes in this complicated ecosystem. Decadal-scale data empowers a growing understanding of the processes that influence metals in the ecosystem, of what to expect when certain conditions occur (high flows, low flows, high winds), and of the ability to apply this understanding to other organisms in the Bay, particularly the fish and bird predators of the clams.