Near-Field Receiving Water Monitoring of Trace Metals and a Benthic Community Near the Palo Alto Regional Water Quality Control Plant in South San Francisco Bay, California: 2005

U.S. GEOLOGICAL SURVEY

OPEN FILE REPORT 2006-1152

Prepared in cooperation with the
CITY OF PALO ALTO, CALIFORNIA

Menlo Park, California

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U.S. DEPARTMENT OF THE INTERIOR
LYNN SCARLETT, Acting Secretary

U.S. GEOLOGICAL SURVEY
PATRICK LEAHY, Acting Director

For Additional Information
Write to: snluoma@usgs.gov

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Samuel N. Luoma, MS 465
U.S. Geological Survey
345 Middlefield Road
Menlo Park, CA 94025

or U.S. Geological Survey
Information Center
Box 25286, MS 517
Denver Federal Center
Denver, CO 80225

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Conversion Factors, Abbreviations, and Acronyms

Conversion Factors

Multiply	By	To obtain
foot (ft)	0.3048	meter
gallon (gal)	3.785	liter (L)
inch (in.)	2.54	centimeter
inch (in.)	25,400	micrometer (µm)
micromolar (µM)	molecular weight	micrograms per liter
micron (µm)	1,000,000	meter
mile (mi)	1.609	kilometer
ounce (oz)	28.35	gram (g)
part per million	1	microgram per gram (µg/g)

Temperature in degrees Celsius (º C) is converted to degrees Fahrenheit (º F) with the following equation:

º F = (1.8 x º C) + 32

Abbreviations and Acronyms

Abbreviations and Acronyms	Meaning
CI	Condition Index
ERL	Effects Range-Low
ERM	Effects Range-Median
ICP-OES	Inductively Coupled Plasma-Optical Emission Spectrophotometry
IRMS	Isotopic Ratio Mass Spectrophotometry
MDL	Method Detection Limit
MLLW	Mean Low Low Water
MRL	Method Reporting Level
NIST	National Institute of Standards and Technology
NPDES	National Pollutant Discharge Elimination System
PARWQCP	Palo Alto Regional Water Quality Control Plant
RWQCB	California Regional Water Quality Control Board
SFEI	San Francisco Estuary Institute
USEPA	U.S. Environmental Protection Agency
USGS	U.S. Geological Survey

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Abstract

Trace elements in sediment and the clam *Macoma petalum* (formerly reported as *Macoma balthica* (Cohen and Carlton 1995)), clam reproductive activity and benthic, macroinvertebrate community structure are reported for a mudflat one kilometer south of the discharge of the Palo Alto Regional Water Quality Control Plant in South San Francisco Bay. This report includes data collected for the period January to December 2005, and extends a critical long-term biogeochemical record dating back to 1974. These data serve as the basis for the City of Palo Alto's Near-Field Receiving Water Monitoring Program, initiated in 1994.

Metal concentrations in both sediments and clam tissue during 2005 were consistent with results observed since 1990. Copper and zinc concentrations in sediment and bivalve tissue displayed a continued decrease over the last decade. In 2005, Cu concentrations were at or below the effects range-low (ERL) concentration (34 µg/g) for the entire year, the first time this has been observed. Also, zinc concentrations never exceeded the ERL (150 µg/g). Yearly average concentrations of copper, zinc and silver in *Macoma petalum* for 2005 were some of the lowest recorded since monitoring for metals began in 1975. The concentrations of mercury and selenium in sediments, during April and January 2004, respectively, were the highest values observed for these elements during this study. Later in 2005, concentrations decreased to historic levels. The increase in mercury and selenium in 2004 was not a permanent trend and concentrations of these elements in sediments and clams at Palo Alto remain similar to concentrations observed elsewhere in the San Francisco Bay.

Analyses of the benthic-community structure of a mudflat in South San Francisco Bay over a 31-year period show that changes in the community have occurred concurrent with reduced concentrations of metals in the sediment and in the tissues of the biosentinal clam *Macoma petalum* from the same area. Analysis of the reproductive activity of *M. petalum* shows increases in reproductive activity concurrent with the decline in metal concentrations in the tissues of this organism. Reproductive activity is presently stable with almost all animals initiating reproduction in the fall and spawning the following spring of most years. The community has shifted from being dominated by several opportunistic species to a community where the species are more similar in abundance, a pattern that suggests a more stable

community that is subjected to less stress. In addition, two of the opportunistic species (*Ampelisca abdita* and *Streblospio benedicti*) that brood their young and live on the surface of the sediment in tubes have shown a continual decline in dominance coincident with the decline in metals. *Heteromastus filiformis*, a subsurface polychaete worm that lives in the sediment, consumes sediment and organic particles residing in the sediment, and reproduces by laying their eggs on or in the sediment has shown a concurrent increase in dominance. These changes in species dominance reflect a change in the community from one dominated by surface dwelling, brooding species to one with species with varying life history characteristics. For the first time since its invasion in 1986, the non-indigenous filter-feeding bivalve *Corbula* (*Potamocorbula*) *amurensis* has shown up in small but persistent numbers in the benthic community.

Introduction

Environmental Monitoring

Determining spatial distributions and temporal trends of metals in sediments and benthic organisms is common practice for monitoring environmental contamination. These data can be the basis for inferring ecological implications of metal contamination. Another common method of environmental monitoring is to examine the community structure of sediment dwelling benthic organisms (Simon 2002). Spatial and temporal changes in community structure reflect the response of resident species to environmental conditions, although the underlying cause(s) for the response may be difficult to identify and quantify. Integrating measurements of metal exposure and biological response can provide a more complete view of anthropogenic disturbances and the associated effects on ecosystem health.

Environmental Exposure to Trace Metals

Sediment particles can strongly bind metals, effectively removing them from solution. As a result, sediments may accumulate and retain metals released to the environment. Thus, concentrations of metals in sediments serve as a record of metal contamination in an estuary, with some integration over time. Fluctuations in the record may be indicative of changes in anthropogenic releases of metals into the environment.

Metals in sediments are also indicative of the level of exposure of benthic animals to metals through contact with and ingestion of bottom sediments and suspended particulate materials. However, geochemical conditions of the sediment affect the biological availability of the bound metals. Assimilation of bioavailable sediment-bound metal by digestive processes and the relative contribution of this source of metals relative to metals in the aqueous phase are not well understood. Thus, in order to better estimate bioavailable metal exposures, the tissues of the organisms themselves may be analyzed for trace metals. Benthic organisms concentrate most metals to levels higher than those that occur in solution. Therefore, the record of tissue metal concentrations can be a more sensitive indicator of anthropogenic metal inputs than the sediment record. Different species concentrate metals to different degrees. However, if one species is analyzed consistently, the results can be employed to indicate trace-element exposures to the local food web. For example, silver (Ag), copper (Cu) and selenium (Se) contamination, originally observed in clams (*Macoma petalum* formerly reported as *Macoma balthica* (Cohen and Carlton 1995)) at the Palo Alto mudflat, was later found in diving ducks, snails, and mussels also from that region (Luoma and others, USGS, unpublished data).

Biological Response to Trace Metals

Contaminants can adversely impact benthic organisms at several organizational levels. For example, responses to a pollutant at the cellular or physiological level of an individual can result in changes at the population level, such as reductions in growth, survival and reproductive success. Community level responses to population level impairment can include overall shifts in species abundance favoring metal-tolerant species that can result in changes in predator/prey interactions, and in competition for available resources. Changes in the benthic community can ultimately result in changes at the ecosystem level due to that community's importance in the cycling of carbon in aquatic environments (see Alpine and Cloern 1992 for a local example).

In all aquatic environments, benthic organisms may be exposed to contaminants at all life stages through a variety of routes - sediment, water and food (see Wang and Fisher 1999 for a summary of the potential transport of trace elements through food). Toxicant exposure is related to contaminant concentration as well as duration. Even at low contaminant levels, long-term exposure can impact benthic organisms. The added complexity of synergistic or antagonistic effects between different contaminants and between contaminants and natural stressors makes the determination of causal relationships difficult to identify and quantify, even on a site-specific basis. However, a time-integrated picture of ecosystem response to contaminant loading can be provided by field studies which link changes in exposure at multiple time scales (in this case seasonal to decadal) to changes at individual, population and community level.

RWQCB and NPDES

The California Regional Water Quality Control Board (RWQCB) has prescribed a Self Monitoring Program with its re-issuance of the National Pollutant Discharge Elimination System (NPDES) permits for South San Francisco Bay dischargers. The recommendation includes specific receiving water monitoring requirements.

Since 1994, the Palo Alto Regional Water Quality Control Plant (PARWQCP) has been required to monitor metals and other specified parameters using sediments and the clam *Macoma petalum* at an inshore location in South San Francisco Bay. In addition to the required monitoring, PARWQCP has undertaken monitoring of the benthic community as a whole. The monitoring protocols have been designed to be compatible with or complement the RWQCB's Regional Monitoring Program. Monitoring efforts are being conducted by the U. S. Geological Survey (USGS) and are coordinated with 30 years of previous data collections and investigations by the USGS at this inshore location.

Objectives

The data presented by this study includes trace-metal concentrations in sediments and clams, clam reproductive activity and benthic-community structure. These data, and those collected in earlier studies, (Hornberger and others 2000a; Luoma and others 1991; 1992; 1993; 1995; 1996; 1997; 1998; Wellise and others 1999; David and others 2002; Moon and others 2003; 2004; Shouse and others 2003; 2004; Thompson and others 2002) were used to meet the following objectives:

- Provide data to assess seasonal and annual trends in trace-element concentrations in sediments and clams, reproductive activity of clams and benthic-community structure at a site designated in the RWQCB's Self-Monitoring Program guidelines for PARWQCP

- Present the data within the context of historical changes in South Bay and within the context of other locations in San Francisco Bay published in the international literature
- Coordinate inshore receiving water monitoring programs for PARWQCB and provide data compatible with relevant aspects of the Regional Monitoring Program. The near-field data will augment the Regional Monitoring Program as suggested by the RWQCB
- Provide data that could support other South San Francisco Bay issues or programs, such as development of sediment quality standards.

Approach

Despite the complexities inherent in monitoring natural systems, the adopted approach has been effective in relating changes in near-field contamination to changes in reproductive activity of a clam (Hornberger and others 2000b) and in benthic-community structure (Kennish 1998). This study, with its basis in historical data, provides a context within which future environmental changes can be assessed.

Metal concentrations were monitored in sediments and a resident species, *Macoma petalum*. Analysis of trace-element concentrations in the sediments provides a record of metal contamination to the site. The concentration and bioavailability of sediment-bound metals are affected by hydrology and geochemical factors (Thomson-Becker and Luoma 1985; Luoma and others 1995). Thus, ancillary data, including grain-size distribution, organic carbon, aluminum and iron content of the sediment, regional rainfall, and surface salinity, were collected to interpret seasonal, annual, and inter-annual variation in metal concentrations. The tissue of *Macoma petalum* provides a direct measure of exposure to bioavailable metals.

Biological response of the benthic community to metal exposure was examined at three levels of organization: individual, population, and community. At the individual level, concentrations of metals in the tissues of *Macoma petalum* were compared with physiological indicators. Two common animal responses to environmental stress are reduced reproductive activity and reduced growth. Growth and reproduction in *M. petalum* occur on fairly regular seasonal cycles. Seasonally, a clam of a given shell length will increase somatic tissue weight as it grows during the late winter and spring. Reproductive tissue increases during the early stages of reproduction, and subsequently declines during and after reproduction. These cycles can be followed with the condition index (CI) which is an indicator of the physiological condition of the animal, and specifically is the total soft tissue weight of a clam standardized to shell length. Inter-annual differences in growth and reproduction, expressed in the CI, are influenced by the availability and quality of food, as well as other stressors such as pollutant exposure and salinity extremes. Earlier studies (Hornberger and others 2000b) have shown that reproductive activity of *M. petalum* has increased with declining metal concentrations in animals from this location. Therefore, CI and reproductive activity of *M. petalum* appear to be useful indicators of physiological stress by pollutants at this location, and continue to be monitored for this study.

At the population level, trends of the dominant benthic species were examined to see if certain species have been more affected than others by environmental change. It has been shown that most taxonomic groups have species that are sensitive to elevated silver (Luoma and others 1995) and that some crustacean and polychaete species are particularly sensitive to elevated sedimentary copper (Morrisey and others 1996, Rygg 1985). Finally, the benthic community was examined for changes in structure (that is, shifts in the species composition of the macroinvertebrate community and abundance of individual species at this site). Prior studies have shown that more opportunistic species are likely to persist in highly disturbed environments (see Nichols and Thompson 1985a). It was hypothesized that a shift in community composition would result from changes in the concentrations of specific metals or in the composite of all contaminants.

Previous analysis of this community has shown no correlation between changes in the community and measured environmental parameters (i.e. salinity, air and water temperature, delta outflow, precipitation, chlorophyll a, sediment total organic carbon, and biological oxygen demand: Shouse 2002). Therefore, the community data was only compared to trace-metal data in this report.

Study Site

The Palo Alto site (PA) is located off of Sand Point on a mudflat on the western shore side of San Francisco Bay (not a slough) (*Figure 1*). The site is one kilometer south of the intertidal discharge point of the PARWQCP. The station is 12 m from the edge of the marsh and 110 cm above mean low low water (MLLW).

The sediment and biological samples from this location reflect a response of the receiving waters to the effluent just beyond the location of discharge. Earlier studies (Thomson and others 1984) have shown that dyes, natural organic materials in San Francisquito Creek and waters in the PARWQCP discharge move predominantly south toward Sand Point and thereby influence the mudflats in the vicinity of Sand Point. Spatial distributions of metal concentrations near the PARWQCP site were described by Thomson and others (1984) (also reported by Hornberger and others 2000a; Luoma and others 1991; 1992; 1993; 1995; 1996; 1997; 1998; Wellise and others 1999; David and others 2002; Moon and others 2003; 2004; Shouse and others 2003; 2004; Thompson and others 2002). Earlier work by Thomson and others (1984) showed that San Francisquito Creek and the Yacht Harbor were minor sources of most trace elements compared to the PARWQCP. The PARWQCP appeared to be the primary source of the elevated metal concentrations at the PA site in the spring of 1980, based upon spatial and temporal trends of Cu, Ag and zinc (Zn) in clams and sediments (Thomson and others 1984; Cain and Luoma 1990). Metal concentrations in sediments and clams (*M. petalum*), especially Cu and Ag, have declined substantially since the original studies as more efficient treatment processes and source control were employed (Hornberger and others 2000b). Frequent sampling each year was necessary to characterize those trends since there was significant seasonal variability (Cain and Luoma 1990; Luoma and others 1985). This report characterizes data for the year 2005, employing the methods described in the succeeding section.

Previous reports (Luoma and others 1995; 1996; 1997; 1998; Wellise and others 1999) also included data for a site in South Bay that that was influenced by discharge from the San Jose/Santa Clara Water Pollution Control Plant (SJ). Samples were collected from this site from 1994 to September 1999. Comparison of data from this site and the Palo Alto site allowed differentiation of local and regional long-term metal trends.

Methods

Sampling Frequency

In dynamic systems such as San Francisco Bay, the environmental effects of anthropogenic stressors are difficult to distinguish from natural seasonal changes. Frequent sampling increases the probability that anthropogenic effects can be identified. Analyses of early data (1974 through 1983; Nichols and Thompson 1985a, 1985b) showed that when differences are small, benthic samples need to be collected at monthly to bimonthly intervals to make the distinction between natural and anthropogenic effects. Therefore, samples were collected, with a few exceptions, on a monthly basis from the exposed mudflat at low tide between January and December 2005. Samples collected in the field included surface sediment, the deposit-feeding clam *M. petalum,* surface water, and sediment cores for community analysis. Surface water, surface sediment and *M. petalum* were not collected during the months of July, August and November. Cores for benthic-community analyses were collected during all months except October and December.

Measurements of Metal Exposure

Sediment

Sediment samples were scraped from the visibly oxidized (brownish) surface layers (top 1-2 cm) of mud. These surface layers represent recently deposited sediments and detritus, or sediments affected by recent chemical reaction with the water column. The sediment also supports microflora and fauna, a nutritional source ingested by *M. petalum.* Sediment samples were immediately taken to the laboratory and sieved through a 100 µm polyethylene mesh with distilled water to remove large grains that might bias interpretation of concentrations. The mesh size was chosen to match the largest grains typically found in the digestive tract of *M. petalum*. All sediment data reported herein were determined from the fraction that passed through the sieve (< 100 µm), termed the silt/clay fraction. Previous studies have shown little difference between metal concentrations in sieved and unsieved sediments when silt/clay type sediment dominates at a site. However, where sand-size particles dominate the bed sediment, differences in metal concentrations can be substantial. Sediments in extreme South San Francisco Bay can vary spatially and temporally in their sand content (Luoma and others 1995; 1996; 1997; 1998; Wellise and others 1999; David and others 2002; Moon and others 2003; 2004 also see SFEI 1997). Where sand content varies, sieving reduces the likelihood that differences in metal concentrations are the result of sampling sediments of different grain size. Some differences between the USGS and the Regional Monitoring Program results (SFEI 1997) reflect the bias of particle size on the latter's data.

To provide a measure of bulk sediment characteristics at a site, and thus provide some comparability with bulk sediment determination such as that employed in the Regional Monitoring Program – San Francisco Estuary Institute (SFEI 1997), the fraction of sediment that did not pass through the sieve (≥100 µm) was determined. This fraction is termed sand fraction. Bulk sediment samples were sieved to determine the percent sand and percent silt/clay (<100 µm) (*Appendix A*). The percentage of the bulk sediment sample composed of sand-sized particles (percent sand) was determined by weighing the fraction of sediment that did not pass through the sieve (≥100 µm), dividing that weight by the total weight of the bulk sample, and multiplying the quotient by 100. The percentage of silt/clay in the sediment was determined similarly by weighing the sediment that passed through the sieve (grain size <100 µm).

The silt/clay fraction was dried at 60º C, weighed, and then subsampled to provide replicates weighing 0.4 to 0.6 gram. These were re-dried (60º C), re-weighed, and then digested by hot acid reflux (10 ml of 16 normal (N) nitric acid) until the digest was clear. This method provides a 'near-total' extraction of metals from the sediment and is comparable with the recommended procedures of the U.S. Environmental Protection Agency (USEPA) and with the procedures employed in the Regional Monitoring Program. It also provides data comparable to the historical data available on San Francisco Bay sediments. While near-total analysis does not result in 100% recovery of all metals, recent comparisons between this method and more rigorous complete decomposition show that trends in the two types of data are very similar (Hornberger and others 1999). After extraction, samples were evaporated until dry, then reconstituted in dilute hydrochloric acid (10 % or 0.6 N). The hydrochloric acid matrix was specifically chosen because it mobilizes silver (Ag) into solution through the creation of Ag-chloro complexes. Sediment extracts were allowed to equilibrate with the hydrochloric acid (minimum of 48 hours) before they were filtered (0.45 µm) into acid-washed polypropylene vials for elemental analysis. Another set of replicate subsamples from the silt/clay fraction were directly extracted with 12 mL of 0.6 N hydrochloric acid (HCl) for 2 hours at room temperature. This partial extraction method extracts metals bound to sediment surfaces and is operationally designed to obtain a crude chemical estimate of bioavailable metal. The extract was pressure filtered (0.45 µm) before elemental analysis.

Organic carbon was determined using a continuous flow isotope ratio mass spectrophotometer (IRMS) (*Appendix A*). Prior to the analysis, sediment samples were acidified with 12 N HCl vapor to remove inorganic carbon.

Water pooled on the surface of the mudflat was collected in a bottle and returned to the lab where it was measured for salinity with a handheld refractometer.

Clam Tissue

Macoma petalum were collected by hand on each sampling occasion. Typically, 60-120 individuals were collected, representing a range of sizes (shell length). As they were collected, the clams were placed into a screw-cap polypropylene container (previously acid-washed) containing site water. These containers were used to transport the clams to the laboratory.

In the laboratory, the clams were removed from the containers and gently rinsed with de-ionized water to remove sediment. A small amount of mantle water was collected from randomly selected clams for the determination of salinity with a refractometer. The salinity of the mantle water and the surface water collected from the site (above) were typically within 1 ppt (‰) of each other. Only surface water values are reported here. Natural sand-filtered seawater (obtained from U.C. Santa Cruz, Long Marine Labs, Santa Cruz, CA) was diluted with de-ionized water to the measured salinity of the site water. Clams were immersed in this water and moved to a constant temperature room (12º C) for 48 hours to allow for the egestion of sediment and undigested material from their digestive tracts. Clams were not fed during this depuration period. After depuration, the clams were returned to the laboratory and further prepared for chemical analysis.

Elemental analysis, excluding mercury and selenium

The shell length of each clam was measured with electronic calipers and recorded digitally. Clams were separated into 1 mm size classes (e.g. 10.0-10.9 mm, 11.0-11.9mm, etc). The soft tissues from all of the individuals within a given size class were dissected from the shell and collected in pre-weighed 20 mL screw-top borosilicate glass vials to form a single composite sample for elemental analysis. The sample for each collection was thus composed of six to ten composites, with each composite consisting of 2 to 19 clams of a similar shell length. The vials were capped with a glass reflux bulb and transferred to convection oven (70ºC). After the tissues were dried to constant weight, they were digested by reflux in sub-boiling 16 N nitric. The tissue digests were then dried and reconstituted in 0.6 N hydrochloric acid for trace-element analysis.

Analysis for mercury and selenium

Samples collected in late winter (January and February), spring (April), and summer (June and September) were analyzed for total mercury (Hg) and selenium (Se). Approximately 40 clams were selected from the collection. The only criterion for selection was that the range of sizes (shell length) within this group was representative of the larger collection. Otherwise the selection of individuals was random. Selected individuals were grouped according to size to form 3-4 composites, each containing a minimum of ~1.25 gram wet weight. To meet this requirement, especially for the smaller clams, the 1-mm size classes were usually combined to form broader size classes (3-4 mm). Once the composites were formed, the clams were dissected as described above, and the soft tissue was placed into pre-weighed 30 mL screw top polycarbonate vials. These vials were closed and transferred to a freezer (-20º C). Once frozen, the samples were freeze-dried. After drying, the samples were shipped to the USGS analytical laboratory in Atlanta, GA where they were prepared and analyzed for selenium and mercury according to the method described by Elrick and Horowitz (1985).

Analytical

Sediment and tissue concentrations of aluminum (Al), chromium (Cr), copper (Cu), iron (Fe), nickel (Ni), silver (Ag), vanadium (V) and zinc (Zn) were determined using Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES). Mercury (Hg) and Selenium (Se) were determined in both sediment and clam tissues by Hydride Atomic Absorption Spectrophotometry. Analytical results are included in *Appendix B*, *Appendix C*, and *Appendix D*.

Quality Assurance

The polypropylene containers used in the field, depuration containers, glass-reflux bulbs, and all glassware and plastic used for metal analysis were first cleaned to remove contamination. Cleaning consisted of a detergent wash and rinse in de-ionized water, followed with a 1 N nitric-acid wash and thorough rinse in double-deionized water (18 MΩ resistivity). Materials were dried in a dust-free positive pressure environment, sealed, and stored in a dust free cabinet.

Samples prepared for ICP-OES analysis (i.e. all elements except selenium and mercury) were accompanied with procedural blanks and standard reference materials issued by the National Institute of Standards and Technology (NIST). Analysis was preceded with instrument calibration, followed by quality-control checks with prepared quality-control standards before, during (approximately every 10 samples) and after each analytical run. Analyses of reference materials (NIST 2079, San Joaquin soils and NIST 2976, mussel tissue) were consistent for the method and generally were within the range of certified values reported by NIST. Recoveries of Cd, Ni, and Pb in NIST 2976 tend to be less than the certified concentrations (*Appendix E*). Method detection limits (MDL) and reporting levels (MRL) were determined using the procedures outlined by Glaser and others (1981), Childress and others (1999), and USEPA (2004) (*Appendix F*). A full quality-assurance/quality-control plan is available upon request.

A variety of standard reference materials were prepared according to the method used for the determination of selenium and mercury. Observed concentrations fell within the range of certified values for these materials (*Appendix D*).

Other data sources

Precipitation data for San Francisco Bay is reported at San Francisco International Airport and was obtained from the California Data Exchange Center 2005.

Biological Response

Condition Index

The condition index (CI) is a measure of the clam's physiological state derived from the relationship between soft tissue weight and shell length and reported as the soft tissue dry weight (grams) for a clam of a particular shell length (mm). Specifically, for each collection, the relationship between the average shell length and tissue dry weight of the composites was fit with a linear regression, and from that regression the tissue dry weight was predicted for a normalized shell length of 25 mm.

Reproductive Activity

A minimum of 10 clams of varying sizes (minimum of 5 mm) were processed for reproductive activity concurrent with samples for metal analyses. Clams were immediately preserved in 10% formalin at the time of collection. The visceral mass of each clam was removed in the laboratory, stored in 70% ethyl alcohol, and then prepared using standard histological techniques. Tissues were dehydrated in a graded series of alcohol, cleared in toluene (twice for one hour each), and infiltrated in a saturated solution of toluene and Paraplast® for one hour, and two changes of melted Tissuemat® for one hour each. Samples were embedded in Paraplast® in a vacuum chamber and then thin sectioned (10 µm) using a microtome. Sections were stained with Harris' hematoxylin and eosin and examined with a light microscope. Each individual was characterized by size (length in mm), sex, developmental stage, and condition of gonads, thus allowing each specimen to be placed in one of five qualitative classes of gonadal development (previously described by Parchaso, 1993) (*Appendix G*).

Community Analysis

Samples for benthic-community analysis were collected with an 8.5 cm diameter x 20 cm deep hand-held core. Three replicate samples were arbitrarily taken, within a square-meter area, during each sampling date.

Benthic-community samples were washed on a 500 µm screen, fixed in 10% formalin and then later preserved in 70% ethanol. Samples were stained with rose bengal solution. All animals in all samples were sorted to species level where possible (some groups are still not well defined in the bay, such as the oligochaetes), and individuals for each species were enumerated. Taxonomic work was performed in conjunction with a private contractor familiar with the taxonomy of San Francisco Bay invertebrates (Susan McCormick, Colfax, CA) (*Appendix H*). S. McCormick also compared and verified her identifications with previously identified samples.

Results and Discussion

Salinity

Surface water salinity is related to the seasonal weather pattern in Northern California, which is characterized by a winter rainy season defined by months with rainfall amounts greater than 0.25 inches (November through April) and a summer dry season (May through October) (*Figure 2*). The 11 year (1994-2005) average annual rainfall is 24.3 inches. At 30.1 inches, precipitation for 2005 was one of the wettest years within this period (rainfall in 1998 was 30.2 inches). Rainfall during March and April of 2005 was especially greater compared to other years.

Surface-water salinity typically exhibits a seasonal pattern that is generally the inverse of regional rainfall (*Figure 3*, *Table 1*). This pattern was again observed in 2005. The salinity minimum of 16 parts per thousand (ppt) occurred in April, consistent with the late season rainfall, and elevated inflow of freshwater from surface water runoff. Considering the cumulative rainfall for the year, the salinity minimum was not as low as in other years of heavy rainfall (e.g. 1997-98). This could indicate that in 2005 winter salinity was affected more by local runoff than by the large flushing flows from the Sacramento/San Joaquin Rivers. Salinities continually increased during the dry season and reached their maximum (26 ppt) in the fall (September-November).

Sediments

Metal concentrations in surface sediments from Palo Alto typically display an annual periodicity of seasonal patterns. Thomson-Becker and Luoma (1985) suggested that this inter-annual variation is related to changes in the size distribution of sediment particles caused by deposition of fine-grained particles in the winter and their subsequent wind-driven re-suspension in the fall. Thomson-Becker and Luoma showed that the composition of surface sediments was dominated by fine-grained particles - and accompanied by high Al and Fe concentrations - during the period of freshwater input (low salinities through April), reflecting annual terrigenous sediment inputs from runoff. Coarser sediments dominated later in the year because the seasonal diurnal winds progressively winnow the fine sediments into suspension through the summer. This pattern was observed again in 2005 (*Figure 4*, *Appendix A*).

In 2005, the percent of silt/clay in the sediment was at its maximum (95%) in April, coincident with prolonged late season rainfall. Aluminum and Fe concentrations varied with the percentage of silt/clay-sized particles (*Figure 4*, *Table 1*), as described above, reflecting the contribution of clays composed of Al and Fe.

The total organic carbon (TOC) content of the sediments varied modestly during the year, coincident with other sedimentary constituents (*Table 1*). TOC content was highest during the winter (January through April values ranged from 1.44 to 1.48 %), after April declined to a minimum in September (0.89%), and then increased during the early winter to 1.23%, as of December 2005. In light of the most recent data, the exceptionally high value observed in October of 2004 (8.1%) appears to have been an anomalous event.

The metals Cr, Ni and V are highly enriched in some geologic formations within the watershed. In North San Francisco Bay, studies of sediment cores indicated that concentrations of these elements similar to those reported here were derived from natural geologic inputs (Hornberger and others, 1999; Topping and Kuwabara, 2003). Inputs of minerals bearing Cr, Ni, and V appear to vary seasonally as suggested by the variable concentrations of these metals in surface sediments. Typically, maximum concentrations coincide with winter/spring maximums in fine sediments, while minimum concentrations occur during the late summer/fall (*Figure 5*, *Table 2*). The minimum Ni concentration in the fall of 2004 (51.7µg/g in October) and the following winter/spring maximum in 2005 (85.3 µg/g in March) were the lowest seasonal concentrations observed since 1994. Concentrations of Cr and V declined from their maximum concentrations in the winter of 2002/2003 to concentrations similar to those prior to 2003.

Copper concentrations in sediments are shown with sediment guidelines set by the National Oceanic and Atmospheric Administration (Long and others, 1995). Long and others defined values between ERL (Effects Range-Low) and ERM (Effects Range-Median) as concentrations that are occasionally associated with adverse effects (21 - 47% of the time for different metals). Values greater than the ERM were frequently associated with adverse effects

(42% - 93% of the time for different metals). It must be remembered, however, that these effects levels were derived mostly from bioassay data and are not accurate estimates of sediment toxicity. In 2005, Cu concentrations were near or below the effects range-low (ERL) (34 µg/g) for the entire year, the first time this has been observed (*Figure 6*, *Table 2*). Cu concentrations were at their maximum (33-35 µg/g) throughout the winter/spring (January to April). The minimum concentration (21 µg/g) was observed in September. The magnitude of the inter-annual cycle was smaller than in some other years (e.g. 2004). Near-total Cu concentrations appear to have been declining gradually since at least 2000. Over the same period, partial-extractable concentrations have remained relatively constant outside of the typical seasonal variation (*Figure 6*).

For the second consecutive year, near-total and partial-extractable Zn concentrations never rose above the Zn ERL (150 µg/g) (*Figure 7*, *Table 2*). Winter Zn concentrations were the lowest observed during the past three years and were consistent with temporal patterns of Cu and Ni over the same period.

The concentration of partial-extractable Ag in Palo Alto sediments are well below the Ag ERL (1 µg/g), but greater than the established concentration for uncontaminated sediments in San Francisco Bay (Hornberger and others, 1999) (*Figure 8*, *Table 2*). A seasonal pattern in Ag concentrations was well defined in 2005, but no long-term trend in this seasonal pattern is evident in the decade prior to 2005.

Mercury concentrations in sediment during 2005 ranged between 0.26 µg/g (September) to 0.32 µg/g (January to April) (*Figure 9*, *Table 2*). These values were more typical of concentrations observed during the record (1994-2005) and were considerably less than the maximum Hg concentrations observed in 2004. The April 2004 concentration of Hg in the sediment (0.49 µg/g) was the highest observed in this study. Otherwise, Hg concentrations were within the range usually observed within San Francisco Bay (0.2 - 0.4 µg/g).

Selenium concentrations were also less during 2005 than in 2004 (*Figure 9*, *Table 2*.) Concentrations ranged between 0.5 µg/g (February) to 0.3 µg/g (June and September). The annual mean concentration for the year was 0.38 ± 0.04 µg/g (*Table 2*), only slightly lower than the overall mean for the entire record (0.40 µg/g).

Clam Tissue

Metal concentrations in the soft tissues of *Macoma petalum* reflect the combined metal exposures from water and food. Exposures to Cu and Ag at Palo Alto are of special interest due to the high tissue concentrations observed at this site in the past relative to other South Bay locations (*Figure 10* and *Figure 11*, *Table 3* and *Table 4*, respectively). During the period 1977 – 1987, the range in annual concentrations of Cu and Ag were 95-287 and 45-106 µg/g, respectively. Since 1987, concentrations have been considerably lower: 24-71 µg Cu /g and 2-20 µg Ag/g. Annual mean concentrations of Cu and Ag for 2005 were, respectively, 26 ± 2 and 1.8 ± 0.3 µg/g, the lowest concentrations (Cu concentrations were comparable in 1991) observed during the record.

Intra-annual variations in metal concentrations in clam soft tissues display a consistent seasonal signal, with fall/winter maxima and spring/summer minima, although it is common for the amplitude of this seasonal cycle to vary from year to year. For example, the winter maxima and the magnitude of seasonal Cu and Ag concentrations were greater between 1994 and 1996 than in subsequent years (*Figure 12*, *Figure13*). The magnitude of the decline in Cu and Ag concentrations during the spring/summer of 2005 was comparable to previous years; however, the subsequent increase in tissue concentrations was not as great as in previous years and as of

December, concentrations were only about half the maximum values observed in 2004. These trends most likely reflect the interaction of the changing exposure regime of the site (the long term decline in metal concentrations) with the annual growth cycle of *M. petalum* (Cain and Luoma 1990).

As with Cu and Ag, tissue concentrations of Cr (*Figure 14*, *Table 5*), Ni (*Figure 15*, *Table 5*) and Zn (*Figure 16*, *Table 5*) also exhibited seasonal cycles. The seasonal cycles of Cr and Ni were very similar in terms of their timing and magnitude throughout the record (1994 - 2005). Neither element exhibited a clear temporal trend (either decreasing or increasing) in concentration. Maximum concentrations occurred in the winter of 1996-1997, while 2000 – 2002 was a period of relatively low winter-maximum concentrations. In 2003, concentrations increased somewhat and have remained relatively comparable through 2005. In addition to the typical seasonal pattern, Zn concentrations exhibited a slight long-term decline in concentration. During 1994-1997, Zn concentrations were notably higher throughout the year when compared to subsequent years. The winter maximum for 2004-05 was somewhat less than the previous two winters, but was comparable to the winter of 2001-02. Wellise and others (1999) observed that seasonal and inter-annual patterns of Cr, Ni, and Zn in *M. petalum* at Palo Alto were generally similar to those from the San Jose site, suggesting that regional-scale processes may be more important than treatment plant inputs in controlling the bioavailability of these elements.

Mercury concentrations in *M. petalum*, like Zn, have trended slightly lower since 1994 (*Figure 17*). The highest concentrations observed during the record occurred in September 1994 (0.53 µg/g) and during the winters of 1995 (0.48 µg/g) and 1996 (0.47 µg/g). The seasonal (summer/fall) low concentration in 1995 (0.33 – 0.37 µg/g) was the highest recorded, also. Concentrations declined after 1996, and since then they have fluctuated seasonally between 0.12 and 0.42 µg/g and averaged 0.26 ± 0.08 µg/g.

Selenium concentrations in *M. petalum* vary seasonally like other elements (*Figure 18*, *Table 5*). Long-term trends in the data are not evident. However, the annual maximum concentrations (during summer/fall) have increased somewhat since 2002. Concentrations in 2005 appear consistent with this more recent feature.

The condition index for *M. petalum* at Palo Alto extends back to 1988 (*Figure 19*). As previously discussed, the data fluctuate seasonally in relation to growth and reproductive cycles, and annual cycles differ in magnitude. For example, the maximum value in the CI during 1994-1999 was generally less than preceding or succeeding years. The CI during 2005 was generally comparable to the previous five years.

Reproduction of Macoma petalum

Earlier studies (Hornberger and others 2000b; Shouse and others 2004) found that low reproductive activity in *M. petalum* in the late 1970s was related to highly elevated concentrations of silver in the soft tissues. This finding has implications for the reproductive success of the population. Following the decline in tissue concentrations of Ag (and Cu) in the 1980s, reproductive activity improved (*Figure 20*) . Furthermore, the low reproductive activity observed during the late 1970s has not been observed during the entire period of reduced metal exposures. Data for 2005 show that *M. petalum* continues to be highly reproductive relative to the 1970's with a high percentage of the animals being reproductively active at any one time and with normal seasonal cycling of reproduction beginning in fall and spawning occurring during the following spring (see *Appendix G* for detailed reproduction data for 2005).

Benthic Community

The simplest metrics that are used in assessing environmental stress on biological communities are estimates of species diversity and total animal abundance. Species diversity, as estimated by a time series of number of species for each month, trended upward in 2005 *(Figure 22)*. However, total animal abundance does not show the same trend *(Figure 23)*. The difficulty with these types of metrics is that they do not consider the possibility that one species can take the place of another. Depending on the characteristics of the new species, the community structure and function may change as a result of this exchange of species. The details of changes in species composition are important because they may reflect the relative ability of species to accommodate environmental stress and redistribute site resources.

Three common bivalves (*Macoma petalum*, *Mya arenaria*, and *Gemma gemma*) did not show any consistent trend over the 29-year period *(Figure 24*, *Figure 25*, and *Figure 26*). In all cases, there was significant seasonal and inter-annual variability in species abundances. There were, however, six species that did show trends in their abundance throughout the study. The first, *Ampelisca abdita*, a small crustacean that lives above the surface of the mudflat in a tube built from selected sediment particles showed a general decline in both the annual average abundances and annual maximum abundances (seasonal peaks in abundance; *Figure 27*). The second species to showed a significant trend was the small polychaete worm *Streblospio benedicti*, which also builds a tube above the surface of the mudflat. As with *A. abdita*, *S. benedicti* exhibited a decline in annual maximum abundances as well as annual average abundances *(Figure 28)*. The small burrowing crustacean *Grandiderella japonica*, a deposit feeder, initially showed a declining trend through the 1980's followed by increasing seasonal maximum abundances in recent years *(Figure 29)*. *Neanthes succinea*, a burrowing polychaete that feeds on surface deposits and scavenges, similarly showed an initial decrease in annual maximum abundances through the 1980's, followed by an increase in both annual average abundances and annual maximum abundances *(Figure 30)*. Two species showed an increase in abundance within the time series. The first was the polychaete worm *Heteromastus filiformis (Figure 31)*, a deposit feeding, burrowing species that lives deep in the sediment (usually 5-20 cm below the surface of the mudflat). Abundance increased sharply in 1985 and then partially receded in the late 1980's. Abundances since 2000 have remained higher than in the late 1970's. The second was an introduced species, *Nippoleucon hinumensis*, a small burrowing crustacean, which appeared in the dataset in 1988 *(Figure 32)* was introduced into the bay in 1986 (Cohen and Carlton 1995). *Corbula amurensis*, a non-indigenous filter feeding bivalve, first appeared in the benthic community as more than a rare species in April 2005 and persisted into November 2005 (Appendix H).

As stated earlier, multivariate analyses of population data of the dominant species with environmental parameters did not reveal any relationships, except with the concentration of silver and copper in the sediment and in the tissue of *Macoma petalum* (using data as reported by David and others 2002). Therefore, this update will only consider those metals (recent data, 2002 through 2003, taken from Moon and others 2004). This comparison can be made by plotting the metals and individual species together over the period of the study. The worm *H. filiformis* has increased in abundance with the decrease in silver and copper through time *(Figure 33)*. Because the natural spatial variability (that is, the large standard deviations around the monthly means) and seasonal variability of invertebrate abundance and metal concentration can be quite large, the annual average abundances for *H. filiformis* and annual average metal concentrations are shown *(Figure 34)* and *(Figure 35)*. To interpret these plots, we must first examine the life history characteristics of this species and determine if there is some mechanism by which this organism could be responding to a decrease in silver or copper in the environment. *H. filiformis* has continual tissue contact with the sediment both at the exterior of its body, as well as within its body, due to its lifestyle of burrowing through the sediment and consuming a diet of mud and organic particles. In addition, this is one of the few species in the present community that reproduces exclusively by laying its eggs in the sediment. The larvae hatch after two to three days and spend two to three days in the plankton before settling back to the mud as juvenile worms (Rasmussen 1956). One hypothesis as to why *H. filiformis* increased in abundance may be that either the adult worms or the eggs are less stressed in the present environment. Because of its mode of reproduction and short planktonic larval period, this species is not likely to move into an area quickly after the environment becomes acceptable. Therefore, it is not possible to identify either the identity of the metal or the threshold concentration of the metal to which the animal is responding without laboratory tests. However, other investigators have shown that silver can adversely affect reproduction in invertebrates and that adult *H. filiformis* can tolerate high levels of copper (Ahn and others1995). The gradual increase in *H. filiformis* abundance through 1984 may be a response to the gradual reduction of metals in the environment or may indicate that it took several years for the population to build up in the area. The large abundance increase in 1985 and 1986, followed by a decline and leveling out of abundance, may be an example of the "boom and bust" principle whereby a species rises to levels too high for the habitat to support, and then declines in abundance until it levels out to a habitat-supportable abundance (Begon and others 1986). It is unclear, based on only eight years of data since the early 1990's, if this species has established a stable abundance.

The two species that have declined in abundance coincident with the decline in metals, the crustacean *A. abdita (Figure 36*, *Figure 37* and *Figure 38)* and the worm *S. benedicti (Figure 39, Figure 40*, and *Figure 41)* have very similar life history characteristics. Both species live on the surface of the sediment in tubes that are built from sediment particles, are known as opportunistic and are thus capable of rapid increase in population size and distribution, brood their young, and produce young that are capable of either swimming or settling upon hatching. It is unclear why these species have become less competitive in the present day environment, but their very low numbers in the last several years indicate that there is a major shift in the community as both species were numerically very dominant in the benthic community in the 1970's and 1980's. Unlike *A. abdita* and *S. benedicti*, there has been no significant decline in the abundance of *G. gemma (Figure 42, Figure 43, and Figure 44)* the small clam that reproduces by brooding their young and lives on the sediment surface. All three species are suspension feeders and thus consume water borne particles, although *S. benedicti* may also deposit feed.

Summary

Long-term Observations

Since 1974, USGS personnel have monitored and conducted basic research on the benthic sediments and biological community in the vicinity of the discharge of the Palo Alto Regional Water Quality Control Plant (PARWQCP). The time series presented here updated previous findings (Luoma and others 1991; 1992; 1993; 1995; 1996; 1997; 1998; Wellise and others 1999; David and others 2002; Moon and others 2003; 2004; 2005, Shouse and others 2003; 2004; Thompson and others 2002) with additional data from January 2005 through December 2005, to create a record spanning 32 years. This long-term dataset includes sediment chemistry, tissue concentrations of metals, condition index and reproductive activity in *Macoma petalum*, and population dynamics of benthic-invertebrate species. The time series encompasses the period when exceptionally high concentrations of copper and silver were found in *M. petalum* (1970's) and the subsequent period when those concentrations declined. The sustained record of biogeochemical data at this site provides a rare opportunity to examine the biological response to metal contamination within this ecosystem.

Studies during the 1970's showed that sediments and *Macoma petalum* at the Palo Alto site contained highly elevated levels of metals, especially Ag and Cu, as a result of metal-containing effluent being discharged from the PARWQCP to South Bay. In the early 1980's, the point-source metal loading from the nearby Palo Alto Regional Water Quality Control Plant was significantly reduced as a result of advanced treatment of influent and source mitigation. Coincident with declines in metal loadings, concentrations of metals in the sediment and in the clam *M. petalum* (serving as a biomonitor of metal exposures) also declined as previously described by Hornberger and others (2000). Hornberger and others found a significant correlation between metal loadings (Cu) and tissue concentrations in *M. petalum*. They also showed that metal levels in sediments and clams respond relatively quickly to changes in metal loading; the reduction in metal loadings by the PARWQCP resulted in a reduction in metal concentrations in both the sediment and *M. petalum* within a year.

Biological responses to metal inputs to South Bay were assessed at different levels of organization. These responses are interpreted within the appropriate temporal context. Because metal exposures were already high when the study began, interpretations are based on observed changes in biological attributes as metal inputs declined. In general, discernable responses at the organism level (i.e. reproductive activity, a manifestation of a cellular or physiological change) to metal exposure may occur within a relatively short time, while population and community level responses take longer to develop. Stable changes in the benthic community may take a relatively long period of time to be expressed because of the normally high degree of intra-annual variability of benthic-community dynamics, which reflects the cumulative response to natural and anthropogenic disturbances. It is therefore critical that sampling frequency and duration be conducted at temporal scales appropriate to characterize the different biological responses.

During the first 10 years of this study, when the metal concentrations were high and declining, the benthic community was composed of non-indigenous, opportunistic species that dominated due to their ability to survive the many physical disturbances on the mudflat (Nichols and Thompson 1985a, 1985b). These disturbances included sediment erosion and deposition, and aerial exposure at extreme low tides, in addition to less well defined stresses. The possible effects of metal exposure as a disturbance factor were not considered in the analyses by Nichols and Thompson as the decline in metal concentrations in *Macoma petalum* and sediment had just begun.

However, data collected throughout the period of declining metal exposure have revealed biological responses. Reproductive activity improved within a year or two of reduced metal exposure, and responses at the population and community levels were observed afterward. Identification of these responses was possible because the frequency of sampling allowed long-term trends related to metal contamination to be identified within the context of repeating seasonal cycles and unrelated inter-annual variation.

2005

In 2005, Cu and Ag concentrations in sediments and the soft tissues of clam *M. petalum* were as low as anytime during the record (that is, since 1974). This is at least partly attributable to the reduced loading of these metals from the treatment plant which was achieved in the 1990s and has been maintained thereafter. For many other elements of regulatory interest, including Cr, V, Ni, and Zn, regional scale factors appeared to influence sedimentary and bioavailable concentrations. Other variables such as precipitation and accelerated erosion of salt marsh banks in recent years, that may influence the seasonal and year to year patterns in sedimentary and tissue concentrations, should still be investigated.

The long-term dataset demonstrates various adverse impacts of contaminants on benthic organisms. Decreasing particulate concentrations of trace metals in the local environment have benefited resident populations of invertebrates, as evidenced by increased reproductive activity in the clam *Macoma petalum* that has been sustained though 2005. The abundances of individual species showed little variability during 2005. This reflects a more stable community in the absence of metal stressors. All dominant species in the community, with the exception of *Gemma gemma*, have abundances similar to those seen in previous years. The lower abundances exhibited by *G. gemma* in 2004 were found elsewhere in the long-term data set, and could be due to a number interdependent factors. The interpretation that shifts in species abundance at Palo Alto were a response to decreasing contaminants continue to be supported by the most recent sediment and community data.

Value of Long-Term Monitoring

This study highlights the importance of long-term ecosystem monitoring. The decadal time series produced during the course of sustained efforts at this site have made it possible to describe trends, identify previously undocumented phenomena, and pose otherwise unrecognized hypotheses that have guided past detailed explanatory studies and can guide future studies. Monitoring studies cannot always unambiguously determine the causes of trends in metal concentrations or benthic-community structure. The strength and uniqueness of this study is the integrated analysis of metal exposure and biological response at intra- and inter-annual time scales over multiple decades. Changes and trends in community structure that may be related to anthropogenic stressors, as was seen in this study, can only be established with a concerted and committed effort of sufficient duration and frequency of sampling. Such rare field designs allow biological responses to natural stressors to be characterized and separated from those introduced by man. Through interpreting time series data, it has been possible to separate anthropogenic effects from natural annual and inter-annual variability. The data from the recent record (that is, within the past decade) increasingly appear to be indicative of an integrated regional ecological baseline with indicators of metal contamination, and greater physiological well-being of aquatic life and benthic-community structure. Changes are occurring in the South Bay watershed. For example, implementation is beginning in the South Bay Salt Ponds Restoration Program; with unknown implications (positive or negative) for all of South Bay. Nannotechnologies, many of which include metal-based products in forms for which we have no experience, are beginning to take hold in consumer products. The long-term, detailed, integrated ecological baseline that has been established at this sampling site will be uniquely valuable in assessing the response of the South Bay environment as our dynamic activities in the watershed continue to change.

References

Ahn, I. Y., Kang, Y. C, and Choi J.W., 1995, The influence of industrial effluents on the intertidal benthic communities in Panweol, Kyeonggi Bay (Yellow Sea) on the west coast of Korea: Marine Pollution Bulletin, v. 30, p. 200-206

Alpine, A. E. and Cloern, J.E., 1992, Trophic interactions and direct physical effects control phytoplankton biomass and production in an estuary: Limnology and Oceanography, v. 37, p. 946-955.

Begon, M., Harper, J. L., and Townsend, C. R., 1986, Ecology: Individuals, populations and communities. Sinauer Associates Inc., Sunderland, Massachusetts.

Cain, D. J. and Luoma, S. N., 1990, Influence of seasonal growth, age and environmental exposure on Cu and Ag in a bivalve indicator, *Macoma balthica* in San Francisco Bay: Marine Ecology Progress Series 60, p. 45-55.

California Data Exchange Center. 2005. San Francisco WB AP. California Department of Water Resources Division of Flood Management. *http://cdec.water.ca.gov/cgi-progs/staMeta?station_id=SFF*.

Childress, C. J. O., Foreman, W. T., Connor, B. F., and Maloney, T. J., 1999, New reporting procedures based on long-term method detection levels and some considerations for interpretations of water-quality data: U.S. Geological Survey Open-File Report 99-193, p. 19.

Cohen, A. N. and Carlton,. J. T., 1995, Biological Study. Nonindigenous aquatic species in a United States Estuary: A case study of the biological invasions of the San Francisco Bay and Delta. U.S. Fish and Wildlife Service, Washington D. C.

David, C. P. C., Luoma, S. N, Brown, C, Cain, D. J, Hornberger, M. and Lavigne, I. R., 2002, Near field receiving water monitoring of trace metals in clams (*Macoma balthica*) and sediments near the Palo Alto Water Quality Control Plant in South San Francisco Bay, California: 1999-2001: *U. S. Geological Survey Open File Report 02-453, 105 p.*

Elrick, K. A. and Horowitz, A. J., 1985, Analysis of rocks and sediments for arsenic, antimony, and selenium, by wet digestion and hydride atomic absorption: *U. S. Geological Survey Open File Report 85-497, 14 p.*

Glaser, J. A., Foerst, D. L., Mckee, G. D., Quave, S. A., Budde, W. L., 1981, Trace analyses for wastewaters: Environmental Science and Technology, v. 15, no. 12, p. 1426-1435.

Hornberger, M. I., Luoma, S. N., Van Geen, A., Fuller, C. C., and Anima, R., 1999, Historical trends of metals in the sediments of San Francisco Bay, California: Marine Chemistry, v. 64, p. 39-55.

Hornberger, M. I., Luoma, S. N., Cain, D., Parchaso, F., Brown, C., Bouse, R., Wellise, C. J., Thompson, J., 2000a, Bioaccumulation of metals by the bivalve *Macoma balthica* at a site in South San Francisco Bay between 1977 and 1997: Long-term trends and associated biological effects with changing pollutant loadings: *U. S. Geological Survey Open File Report 99-55, 42 p.*

Hornberger, M., Luoma, S., Cain, D., Parchaso, F., Brown, C., Bouse, R., Wellise, C., Thompson, J., 2000b, Linkage of bioaccumulation and biological effects to changes in pollutant loads in South San Francisco Bay: Environmental Science and Technology, v. 34, p. 2401-2409.

Kennish, J. K., 1998, Pollution impacts on marine biotic communities: CRC Press, New York. 310 p.

Long, E. R., MacDonald, D. D., Smith, S. L., and Calder, F. D., 1995, Incidence of adverse biological effects within ranges of chemical concentrations in marine and estuarine sediments: Environmental Management, v. 19, p. 81-97.

Luoma, S. N., Cain, D. J., and Johansson, C., 1985, Temporal fluctuations of silver, copper and zinc in the bivalve *Macoma balthica* at five stations in South San Francisco Bay: Hydrobiologia, v. 129, p. 109-120.

Luoma, S. N., Cain, D. J., Brown, C. and Axtmann, E. V., 1991, Trace metals in clams (*Macoma balthica*) and sediments at the Palo Alto Mudflat in South San Francisco Bay: April, 1990 - April, 1991: *U. S. Geological Survey Open File Report 91-460*, 47p.

Luoma, S. N., Cain, D. J., Brown, C. and Hornberger, M., 1992, Trace metals in clams (*Macoma balthica*) and sediments at the Palo Alto Mudflat in South San Francisco Bay: May 1991 - May 1992: *U. S. Geological Survey Open File Report 92-456*, 51p.

Luoma, S. N., Cain, D. J., Brown, C. and Hornberger, M., 1993, Trace metals in clams (*Macoma balthica*) and sediments at the Palo Alto Mudflat in South San Francisco Bay: June 1992 - June 1993: *U. S. Geological Survey Open File Report 93-500*, 52p.

Luoma, S. N., Cain, D. J., Brown, C. and Hornberger, M., 1995, Near field receiving water monitoring of trace metals in clams (*Macoma balthica*) and sediments near the Palo Alto and San Jose/Sunnyvale Water Quality Control Plants in South San Francisco Bay: June 1993 - October 1994: *U. S. Geological Survey Open File Report 95-299*, 83p.

Luoma, S. N., Cain, D. J., Brown, C., Hornberger, M., and Bouse, R. 1996, Near field receiving water monitoring of trace metals in clams (*Macoma balthica*) and sediments near the Palo Alto and San Jose/Sunnyvale Water Quality Control Plants in South San Francisco Bay: December 1994 - December 1995: *U. S. Geological Survey Open File Report 96-203*, 90p.

Luoma, S. N., Cain, D. J., Brown, C., Hornberger, M., and Bouse, R. 1997, Near field receiving water monitoring of trace metals in clams (*Macoma balthica*) and sediments near the Palo Alto and San Jose/Sunnyvale Water Quality Control Plants in South San Francisco Bay: 1996: *U. S. Geological Survey Open File Report 97-585*, 91p.

Luoma, S. N., Ho, Y.B, and. Bryan, G. W., 1995, Fate, bioavailability and toxicity of silver in estuarine environments: Marine Pollution Bulletin, v. 31, p. 44-54.

Luoma, S. N., Wellise, C, Cain, D. J., Brown, C., Hornberger, M., and Bouse, R., 1998, Near field receiving water monitoring of trace metals in clams (*Macoma balthica*) and sediments near the Palo Alto and San Jose/Sunnyvale Water Quality Control Plants in South San Francisco Bay: 1997: *U. S. Geological Survey Open File Report 98-563*, 88p.

Morrisey, D.J., Underwood, A. J., and Howitt, L., 1996, Effects of copper on the faunas of marine soft-sediments: an experimental field study: Marine Biology, v. 125, p.199-213.

Moon, E., David, C. P. C., Luoma, S. N, Cain, D. J, Hornberger, M. and Lavigne, I. R., 2003, Near field receiving water monitoring of trace metals in clams (*Macoma balthica*) and sediments near the Palo Alto Water Quality Control Plant in South San Francisco Bay, California: 2002: *U.S. Geological Survey Open File Report 03-339*, 78p.

Moon, E., Luoma, S. N, Cain, D. J, Hornberger, M. and David, C. P. C., 2004, Near field receiving water monitoring of trace metals in clams (*Macoma balthica*) and sediments near the Palo Alto Water Quality Control Plant in South San Francisco Bay, California: 2003: *U.S. Geological Survey Open File Report 2004-1213*, 84p.

Nichols, F. N. and Thompson, J. K., 1985a, Persistence of an introduced mudflat community in South San Francisco Bay, California: Marine Ecology Progress Series, v. 24, p. 83-97.

Nichols, F. N. and Thompson, J. K., 1985b, Time scales of change in the San Francisco Bay benthos: Hydrobiologia, v. 129, p. 121-138.

Parchaso, F., 1993, Seasonal reproduction of *Potamocorbula amurensis* in San Francisco Bay, California: M.S. Thesis, San Francisco State University, San Francisco, CA.

Rasmussen, E., 1956, The reproduction and larval development of some polychaetes for the Isefjord, with some faunistic notes: Biol. Meddr., v. 23, no. 1, p.1-84.

Rygg, B., 1985, Effect of sediment copper on benthic fauna: Mar. Ecol. Prog. Ser., v. 25, p. 83-89.

SFEI (San Francisco Estuary Institute), 1997, RMP, Regional Monitoring Program for Trace Substances: 1996: Richmond, CA, 349 p.

Shouse, M. K., 2002, The effects of decreasing trace metal concentrations on benthic community structure: M.S. Thesis, San Francisco State University, San Francisco, CA, 177p.

Shouse, M. K., Parchaso, F., and Thompson, J. K., 2004, Near-field receiving water monitoring of benthic community near the Palo Alto Water Quality Control Plant in South San Francisco

Bay: February 1974 through December 2003: *U.S. Geological Survey Open File Report 2004-1210*, 39p.

Shouse, M.K., F. Parchaso, and J.K. Thompson. 2004. Near-field receiving water monitoring of benthic community near the Palo Alto Water Quality Control Plant in South San Francisco Bay: February 1974 through December 2003. *U.S. Geological Survey Open File Report 2004-1210*, Menlo Park, California, 39pp.

Simon, T. P., 2002, Biological response signatures: CRC Press, Boca Raton, FL.

Thomson, E. A., Luoma, S. N., Johansson, C. E., and Cain, D. J., 1984, Comparison of sediments and organisms in identifying sources of biologically available trace metal contamination: Water Research, v. 18, p. 755-765.

Thompson, J. K., Parchaso, F., and Shouse, M. K., 2002, Near field receiving water monitoring of benthic community near the Palo Alto Water Quality Control Plant in South San Francisco Bay: February 1974 through December 2000: *U.S. Geological Survey Open File Report 02-394*, 117p.

Thomson-Becker, E. A., and Luoma, S. N., 1985. Temporal fluctuations in grain size, organic materials and iron concentrations in intertidal surface sediment: Hydrobiologia, v. 129, p. 91-109.

Topping, B. R. and Kuwabara, J. S., 2003, Dissolved nickel and benthic flux in south San Francisco Bay: A potential for natural sources to dominate: Bull. Environ. Toxicol. Chem. v. 71, p. 46-51.

U.S. Environmental Protection Agency Office of Water, 2004, Revised Assessment of Detection and Quantitation Approaches, EPA-821-B-04-005, U.S. Environmental Protection Agency, 1200 Pennsylvania Avenue, NW Washington, DC 20460, 254p.

Wang, W. and Fisher, N. S., 1999, Delineating metal accumulation pathways for marine invertebrates: Sci. Total Environ., v. 237, p. 459-472.

Wellise, C., Luoma, S. N., Cain, D. J., Brown, C., Hornberger, M., and Bouse, R., 1999, Near field receiving water monitoring of trace metals in clams (*Macoma balthica*) and sediments near the Palo Alto and San Jose/Sunnyvale Water Quality Control Plants in South San Francisco Bay: 1998: U.S. *Geological Survey Open File Report 99-455, 101pp*.

Figures

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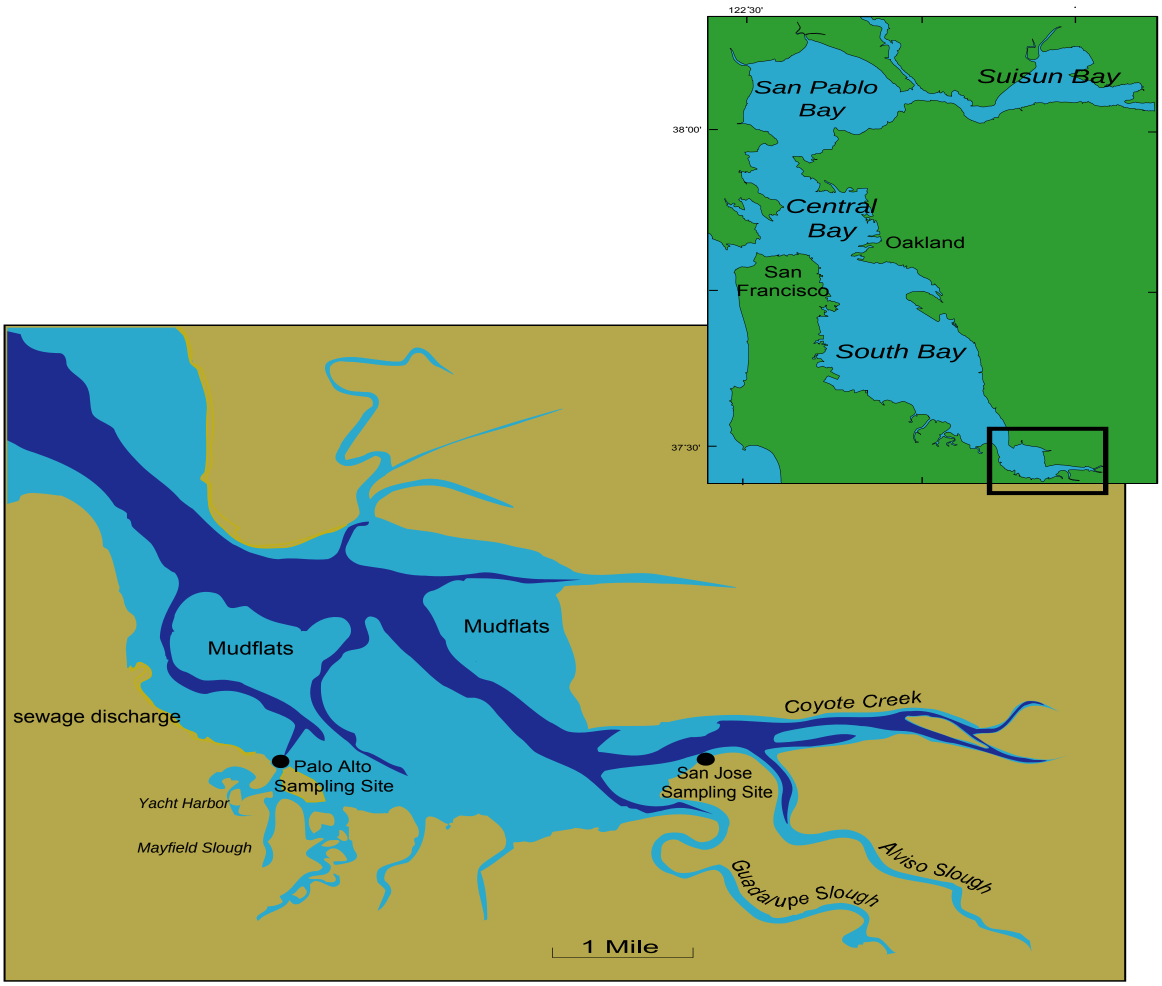

Figure 1. Location of the Palo Alto sampling site in South San Francisco Bay.

The intertidal zone is shaded light blue, subtidal in dark blue, and shoreline in brown. Effluent from the Palo Alto Regional Water Quality Control Plant is discharged approximately 1 mile north/west of the sampling site. The San Jose sampling site (inactive) also is shown for reference.

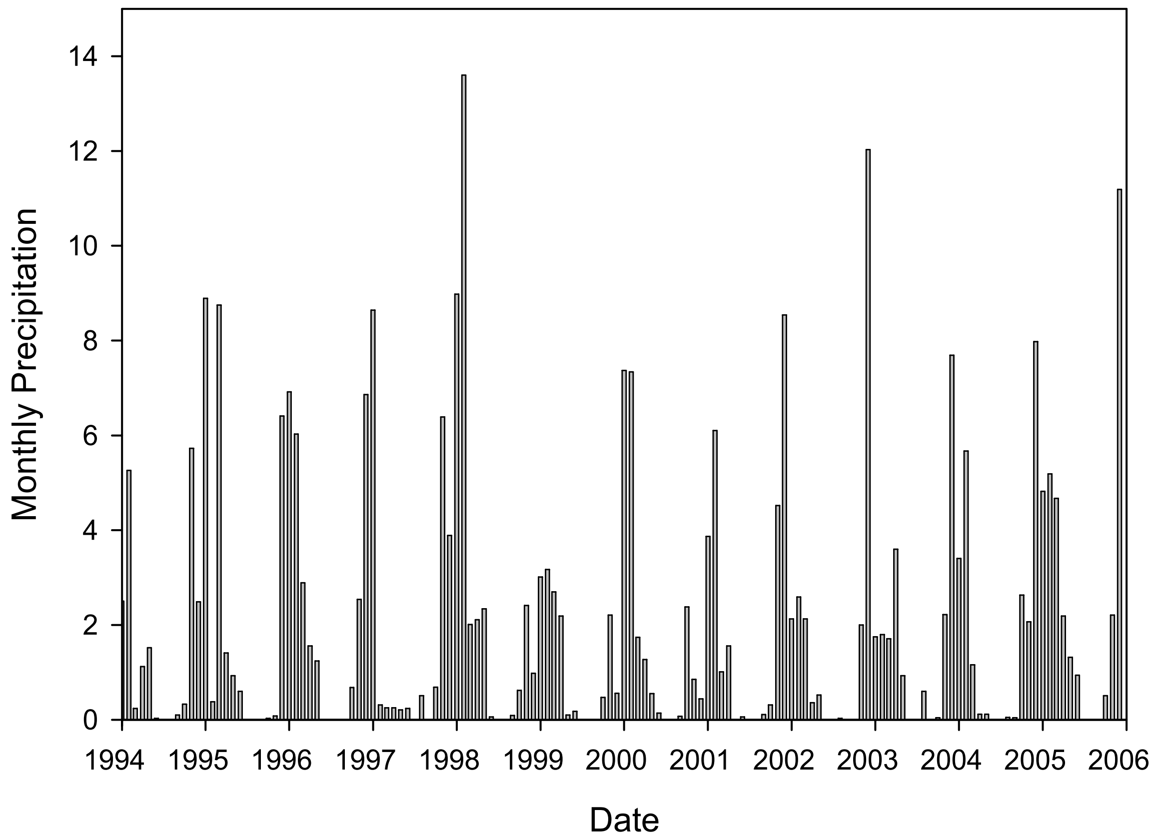

Figure 2. Precipitation

Data from San Mateo gauge station is for period from 1994 through 2005. Precipitation is in inches.

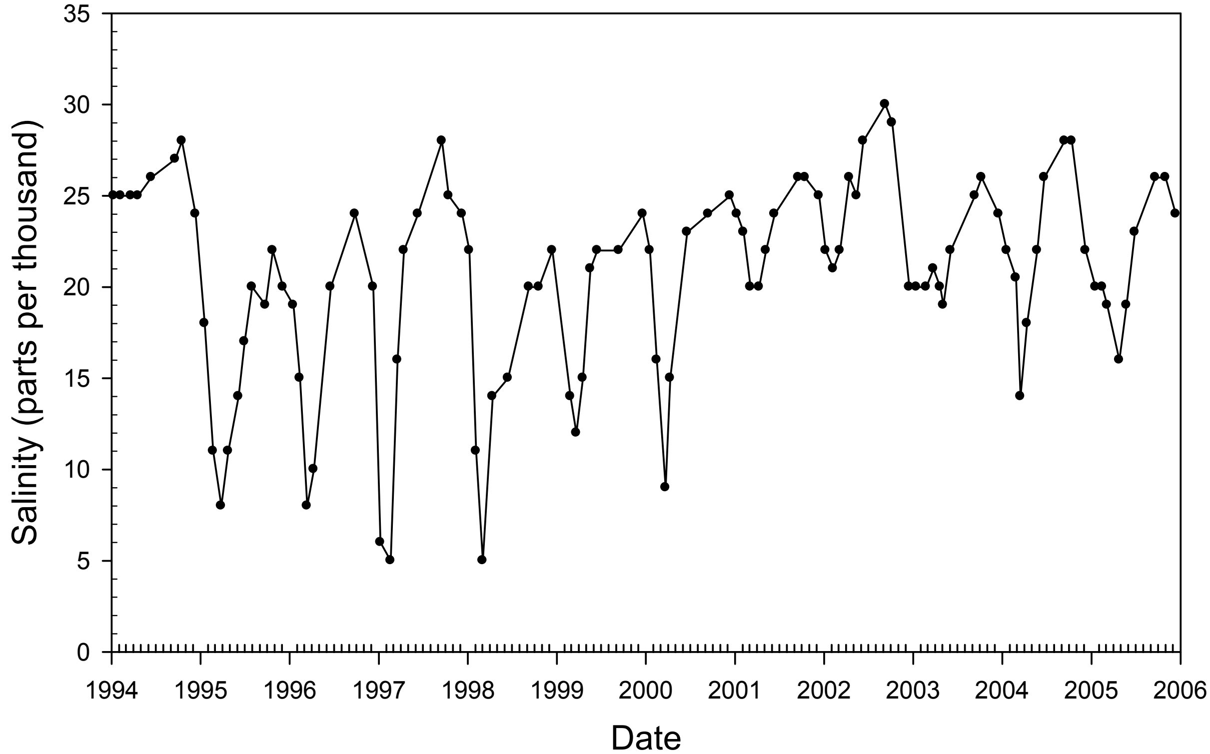

Figure 3. Water column salinity

Data from Palo Alto site is for period from 1994 through 2005.

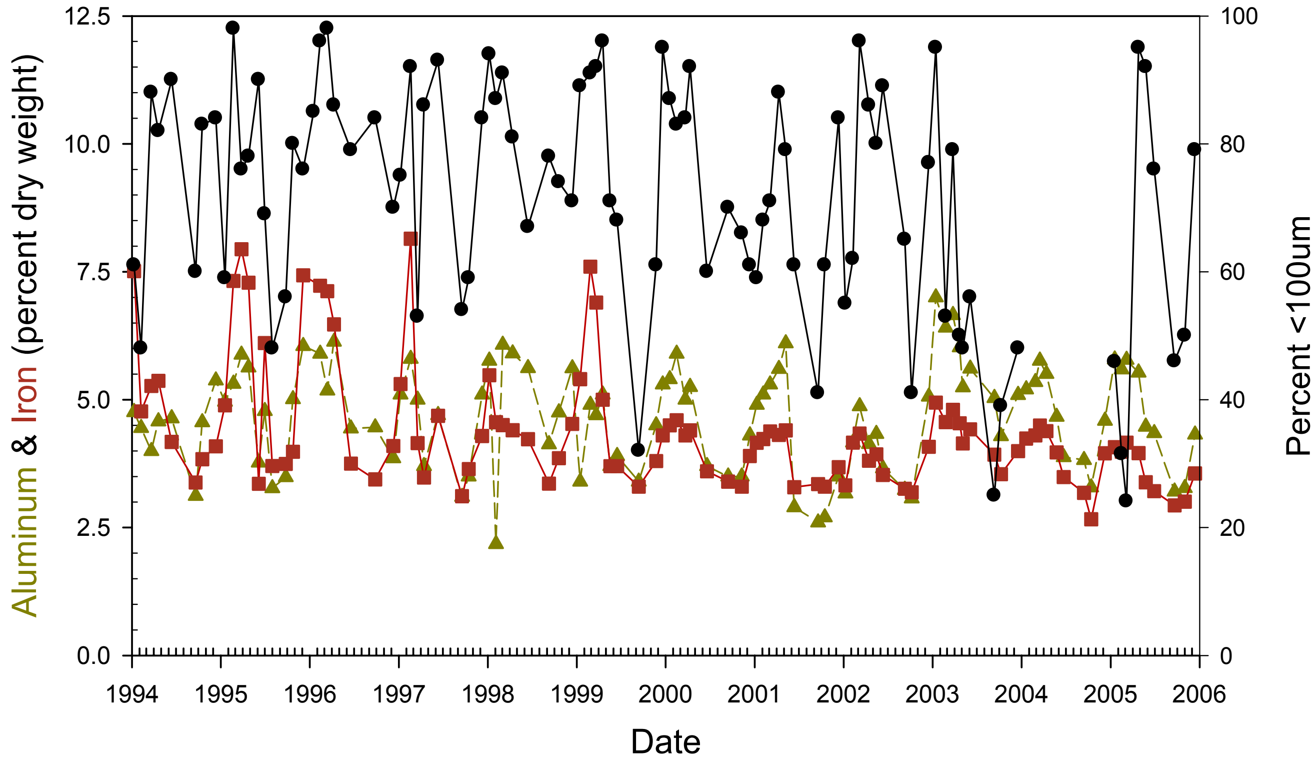

Figure 4. Aluminum, iron and silt/clay in sediments

Data are for the period from 1994 through 2005. Percent aluminum (▲), iron (■) and silt/clay (●) extracted by near-total digest. Data for percent fines for 2004 contain unquantifiable biases due to errors in sample processing, and therefore have been censored. Data for 2004 are shown in Appendices A-2 and A-3 for qualitative purposes only.

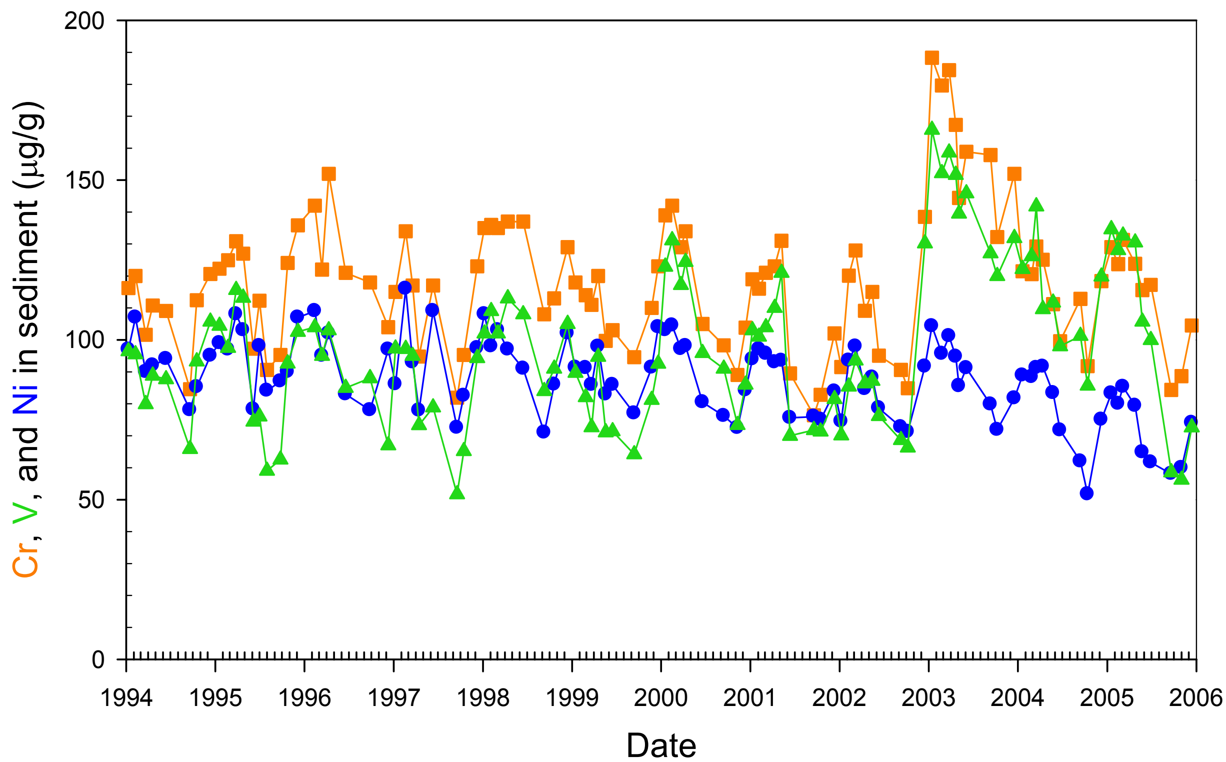

Figure 5. Chromium, nickel and vanadium in sediments

Data are for the period from 1994 through 2005. Concentrations of chromium (Cr) (■), nickel (Ni) (●) and vanadium (V) (▲) extracted by near-total digest.

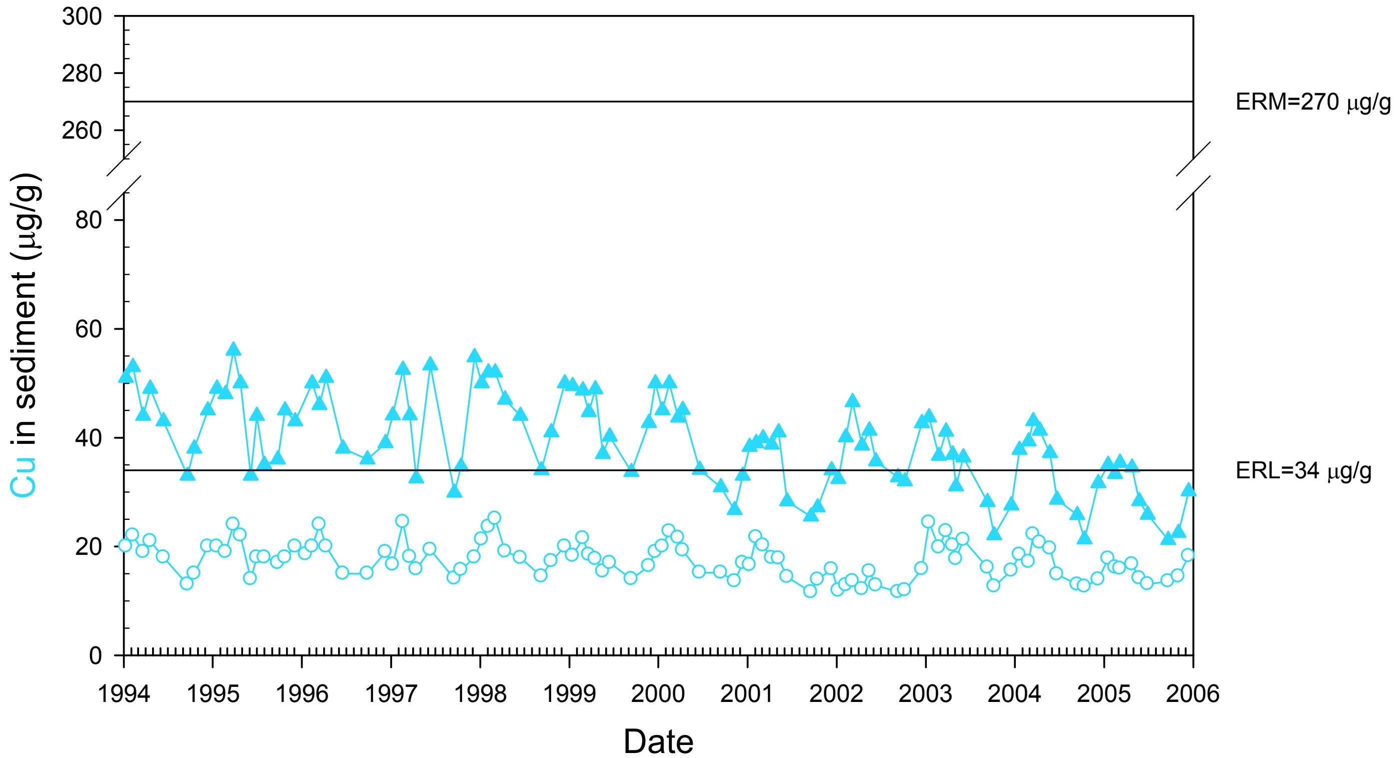

Figure 6. Copper in sediments

Data are for the period from 1994 through 2005. Near-total (▲) and partial-extractable (○) copper.

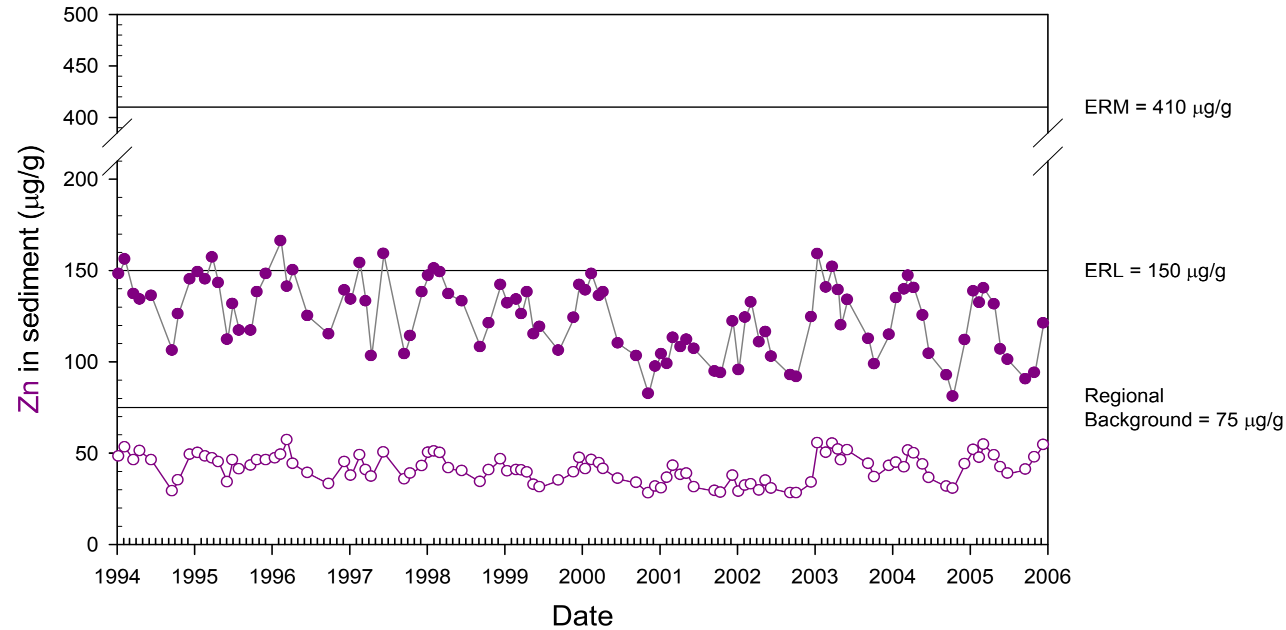

Figure 7. Zinc in sediments

Data are for the period from 1994 through 2005. Near-total (●) and partial-extractable (○) zinc.

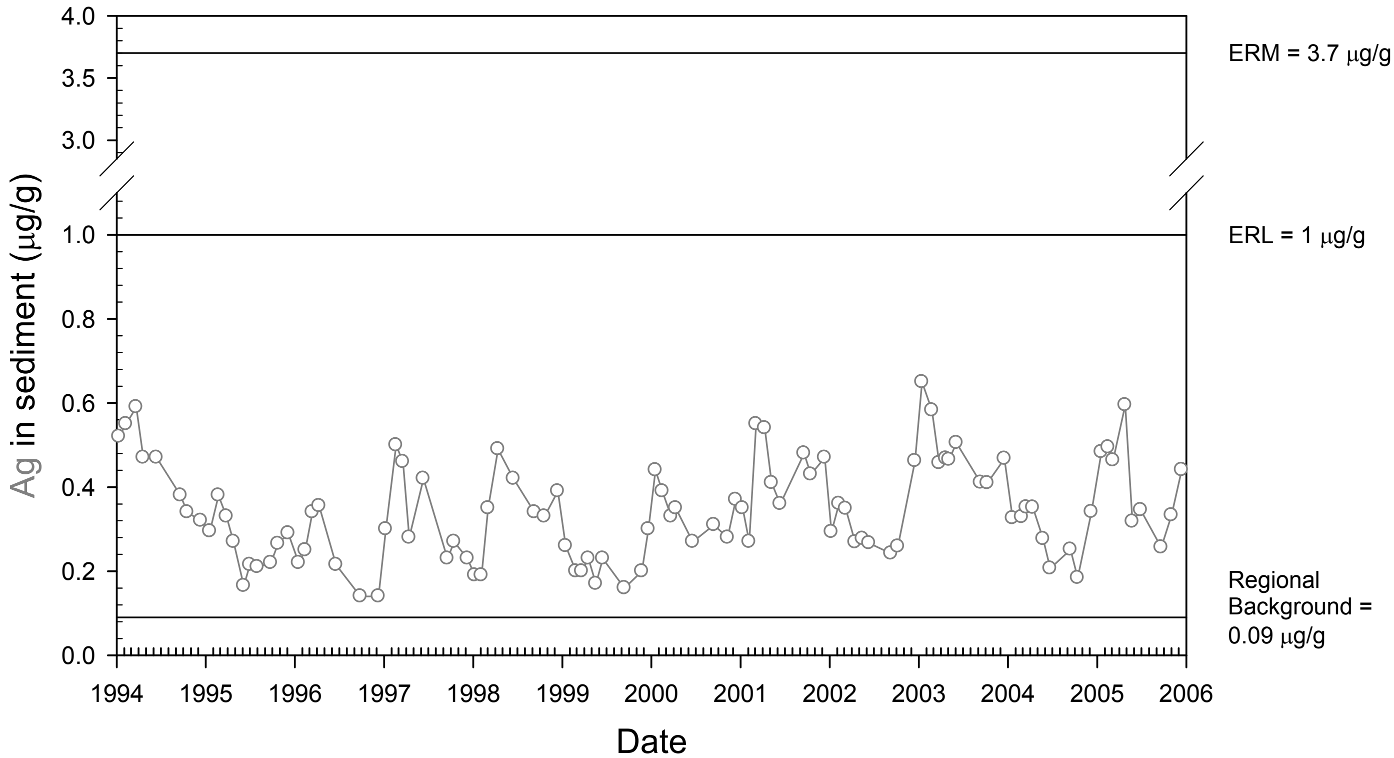

Figure 8. Silver in sediments

Data are for the period from 1994 through 2005. Data represent partial-extractable silver (treatment with 0.6 N hydrochloric acid).

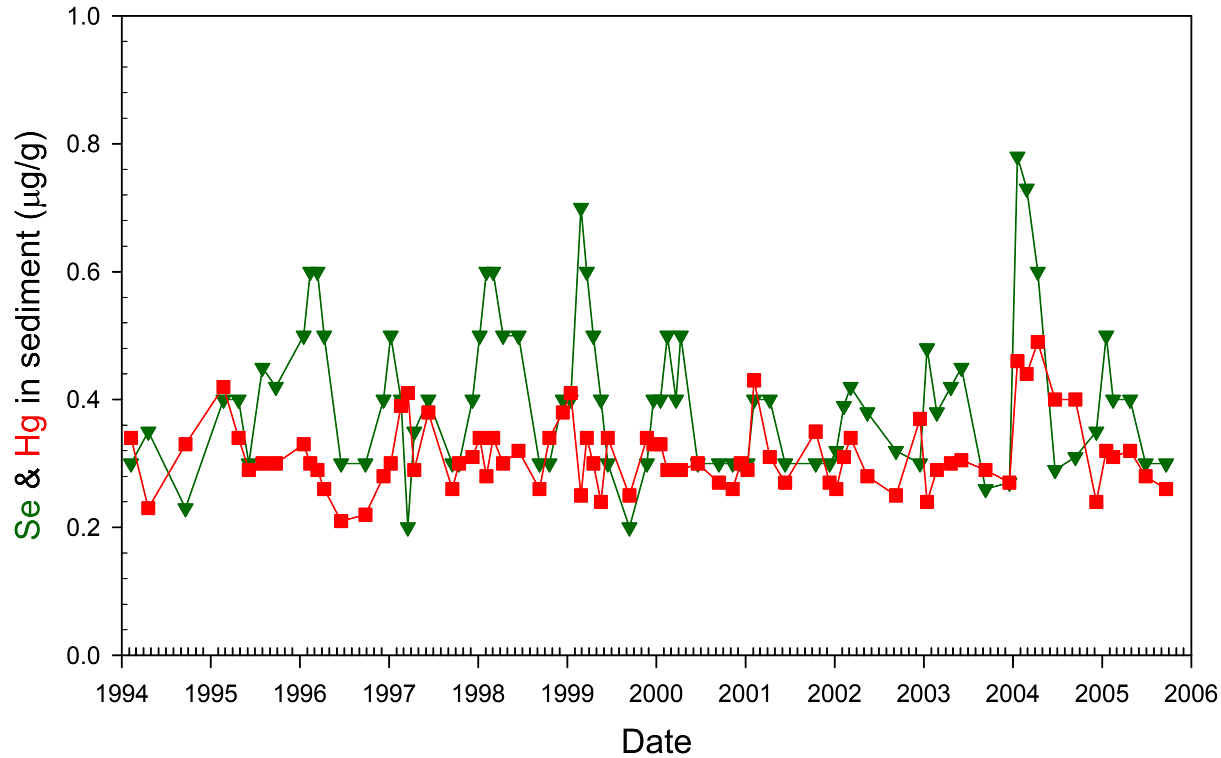

Figure 9. Selenium and mercury in sediments

Data are for the period from 1994 through 2005. Selenium (▼); mercury (■).

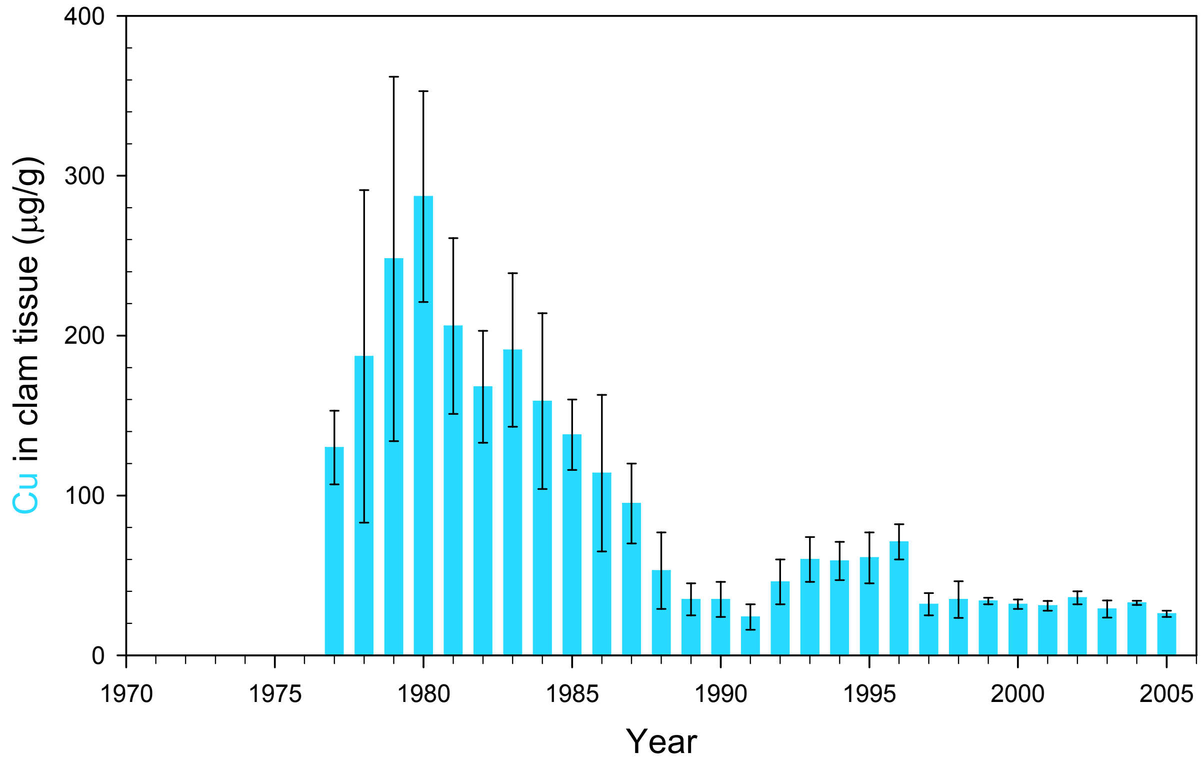

Figure 10. Annual mean copper in *Macoma petalum*

The period of record is from 1977 through 2005. The error bars are the standard error of the mean (SEM).

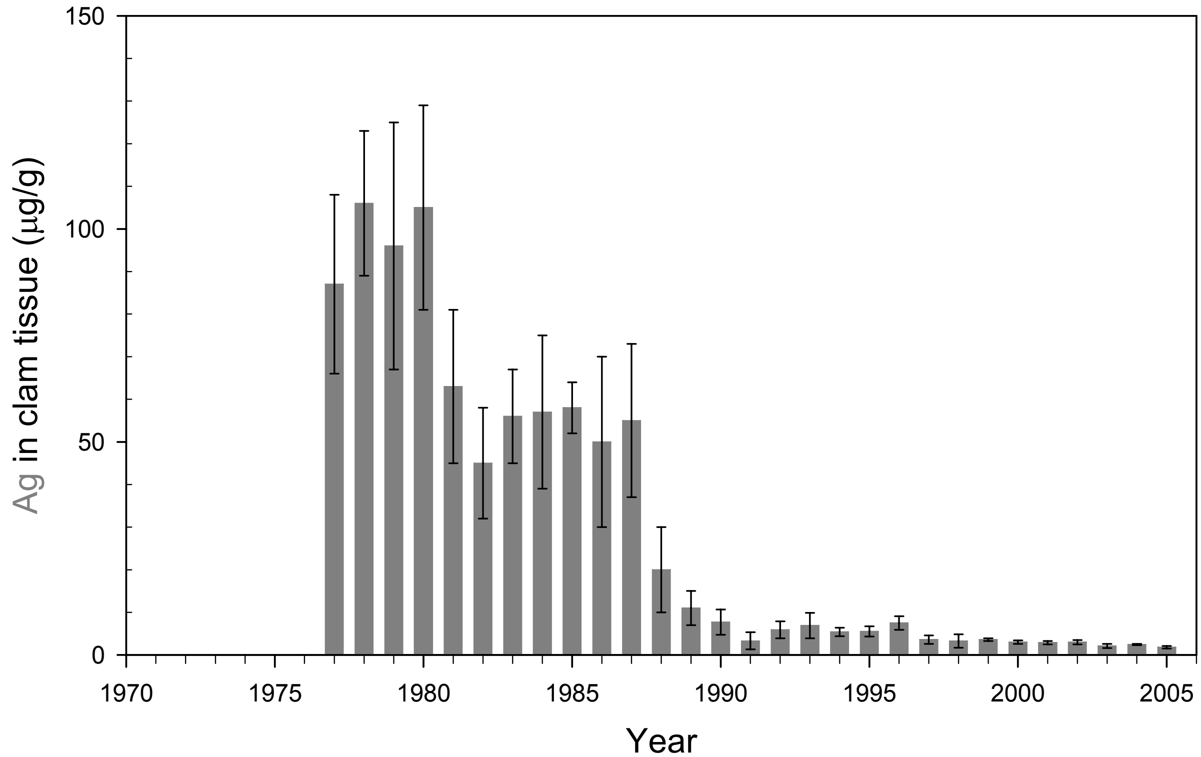

Figure 11. Annual mean silver in *Macoma petalum*

The period of record is from 1977 through 2005. The error bars are the standard error of the mean (SEM).

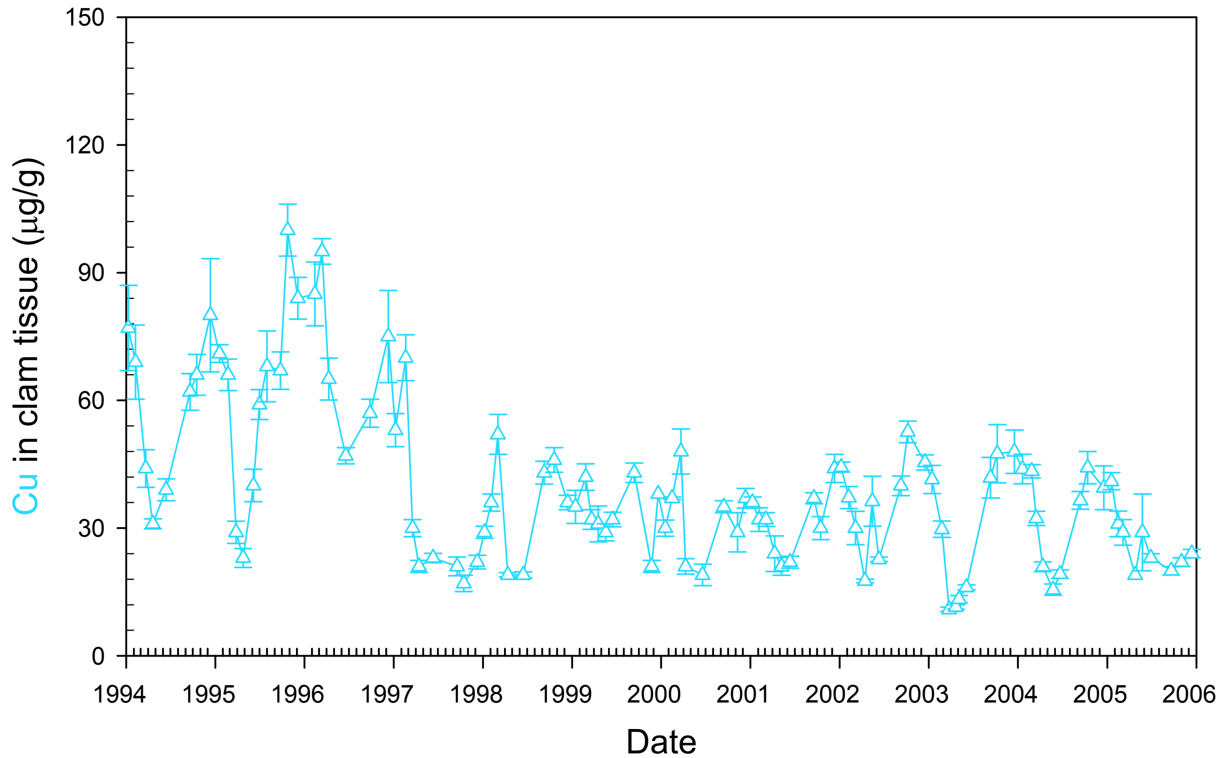

Figure 12. Copper in *Macoma petalum*

Each value is the mean concentration for the sample collected on a given date. The error bar is the standard error of the mean (SEM).

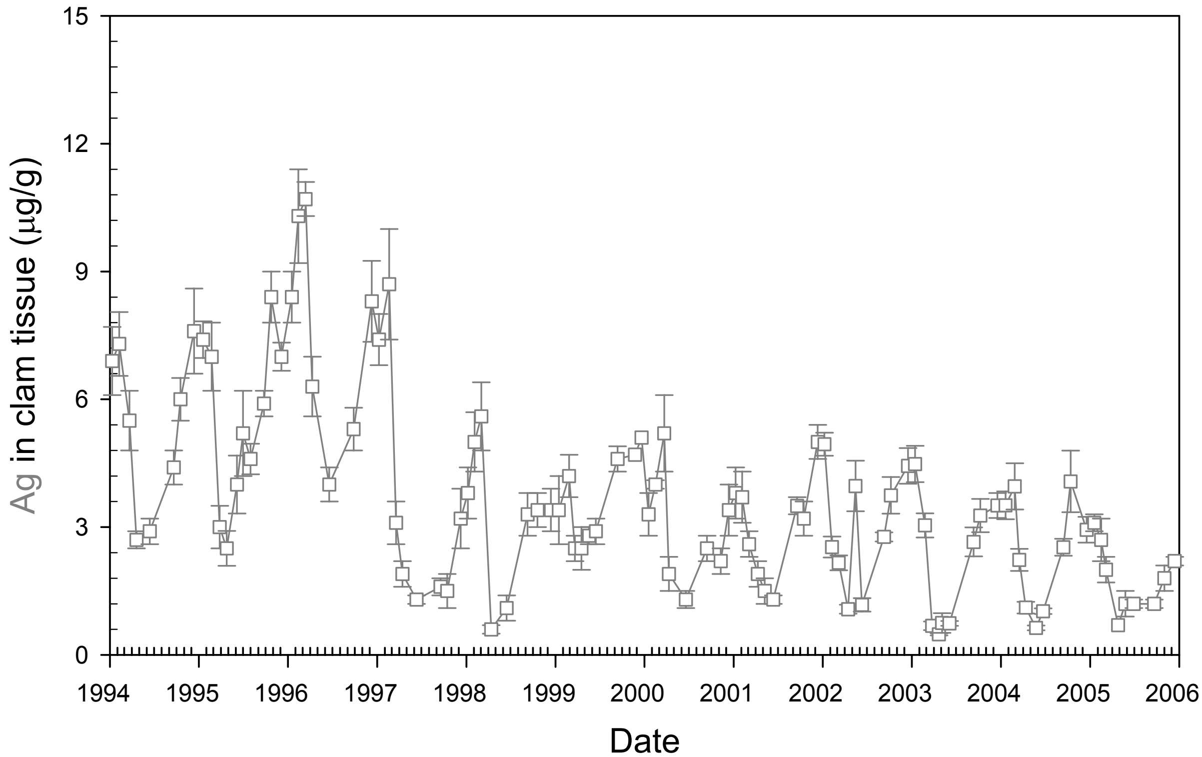

Figure 13. Silver in *Macoma petalum*

Each value is the mean concentration for the sample collected on a given date. The error bar is the standard error of the mean (SEM).

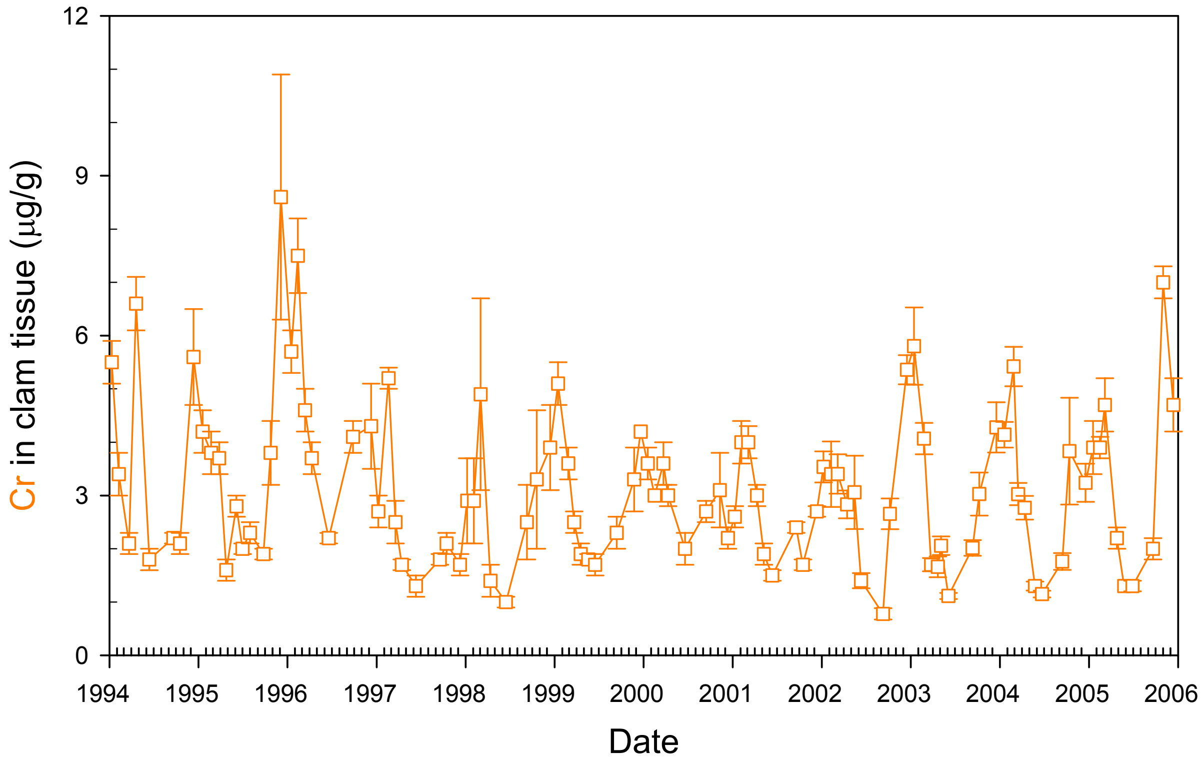

Figure 14. Chromium in *Macoma petalum*

Each value is the mean concentration for the sample collected on a given date. The error bar is the standard error of the mean (SEM).

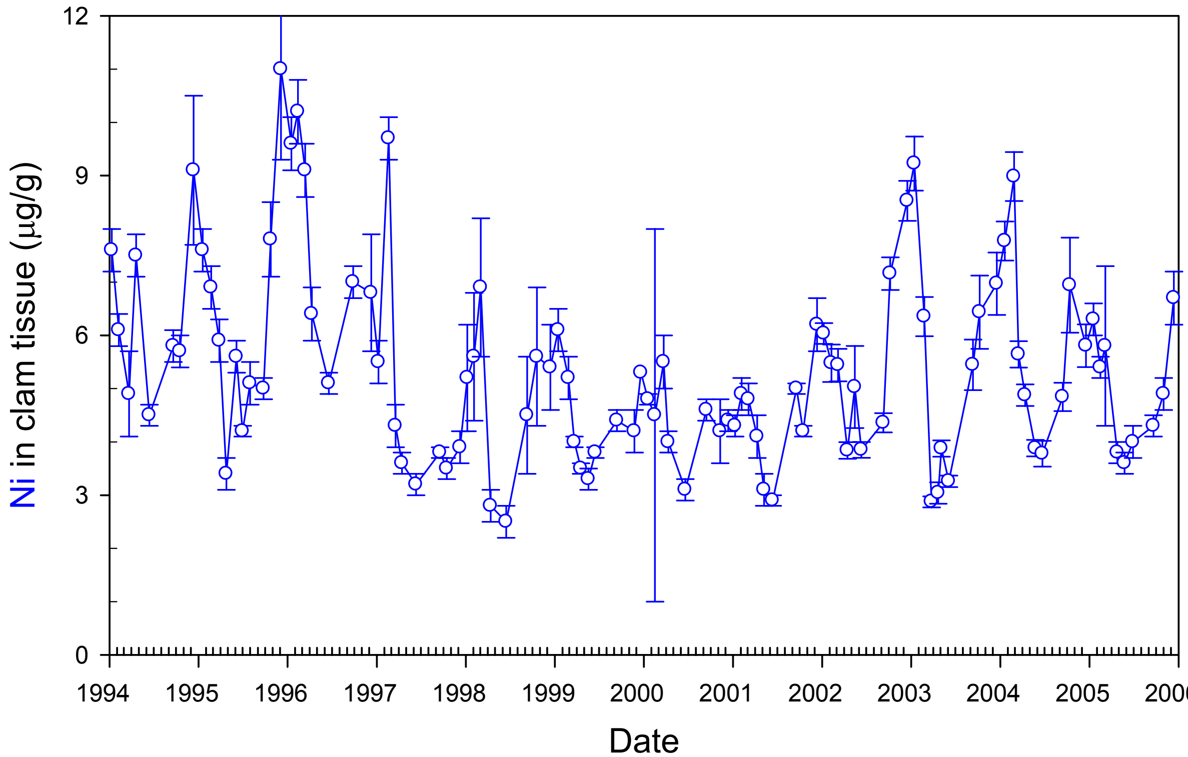

Figure 15. Nickel in *Macoma petalum*

Each value is the mean concentration for the sample collected on a given date. The error bar is the standard error of the mean (SEM).