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Distribution, Variability, and Impacts of Trace Elements in San Francisco Bay

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Studies conducted to date in San Francisco Bay suggest that the trace elements of greatest concern are Ag, Cu, Se, Cd, and perhaps Hg. The distributions of these elements in the Bay are complex, as are temporal trends. Neither spatial nor temporal variability are fully documented. However, certain locations are considerably metal-enriched, coincident with locations of anthropogenic element input. Some evidence suggests that trace elements may exert detrimental impacts on benthic species in contaminated localities. Broad scale impacts will be difficult to determine without a fundamental understanding of ecological processes and a systematic description of the frequency of patches of metal disturbance in the Bay.

San Francisco Bay has undergone important physical and biological changes since the mid-1800s (Nichols *et al.*, 1986). Many of those changes are probably of significance to trace element behaviour within the estuary, although links between specific changes and specific effects are poorly understood. For example, the major rivers entering the Bay have been drastically modified for water management; 60% of the historic freshwater inflow is diverted, mostly for agricultural use, before it reaches the estuary (Nichols *et al.*, 1986). Hydrodynamic changes resulting from loss of freshwater input have implications for trace element inputs and residence times within the Bay system (e.g Luoma & Cloern, 1982). Destruction of 95% of the marshes (Atwater, 1979) and retention of fine-grained sediments originally mobilized by hydraulic gold-mining (Gilbert, 1917) also could affect metal transport and assimilation. Nearly all the common macroinvertebrates present on the inner shallows of the bay, some planktonic invertebrates and algae, and a substantial proportion of the fish species that compose the modern biological community of the Bay were introduced through human activities (Carlton, 1979; Nichols & Thompson, 1985; Leidy & Fiedler, 1985). The hardy, adaptable, temporally variable and spatially patchy nature of this community (Nichols, 1979) adds to the difficulty of understanding biological changes that might have been caused by trace elements. Quantitative study of trace elements in San Francisco Bay began in the early 1970s. However, the issues raised by the two decades of available data must be assessed within the context of the century of radical change that preceded their collection. A more comprehensive consideration of the data available for specific elements is presented elsewhere (Phillips, 1987).

Inputs

The largest mass of trace element input to San Francisco Bay comes from the major river systems (Table 1; also see Fig. 2, Wright & Phillips, this issue for map). Historically, trace element releases to the rivers probably accelerated soon after the discovery of gold in the Sierra Nevada in 1848 (quantitative data are not available, of course). Copper, zinc, silver, gold, and mercury all were mined actively on the Sacramento and San Joaquin Rivers in the late 1800s (Kinkel *et al.*, 1956). Mercury also was extensively employed in the placer gold mining operations, resulting in direct release of an estimated 3500 t of the element to streams and

TABLE 1

Inputs of trace elements to San Francisco Bay (in kg d^{-1}) from municipal and industrial point sources, urban runoff and the Sacramento–San Joaquin River system. Ratios of point source inputs and total anthropogenic input (sum of point source and urban runoff) relative to riverine input also are shown. Data from Gunther *et al.*, 1987.

	Point source	Urban runoff	Rivers	Point source riverine	Anthropogenic riverine
Ag	7.5	?	26	0.28	>0.28
As	5.7	9	37	0.15	0.39
Cd	4.0	3	27	0.15	0.26
Cr	14	15	92	0.15	0.32
Cu	31	59	203	0.15	0.44
Hg	0.8	0.2	3	0.26	0.33
Ni	29	?	82	0.35	>0.35
Pb	17	250	66	0.26	4.0
Se	2.5	?	7.4	0.33	>0.33
Zn	74	268	288	0.25	1.19

rivers. Today, fish kills caused by runoff from minespoils occasionally occur in the Shasta Lake region of the Sacramento River (Nordstrom *et al.*, 1977), and metal enrichment in fish tissues in streams and rivers that once received mine wastes is common (Woodard, 1979). Despite the upstream enrichment, it is not clear whether present day trace element inputs to the estuary from the rivers are greater than their historic levels. Element concentrations in solution and suspension at the head of the estuary are not unusually enriched (see later discussion); and the high loadings to the estuary primarily are the result of a large sediment load and massive volumes of inflow.

Since the mid-1800s urbanization and industrialization have grown to surround San Francisco Bay itself. The Bay now differs from systems such as the Chesapeake in that most modern anthropogenic inputs of trace elements originate from sources on the estuary, rather than on the incoming rivers. The most significant characteristic of the local sources of trace elements is their number and their diversity. Fifty municipal waste water treatment plants discharged approximately 2.9×10^9 l d^{-1} of effluent into the Bay and its delta in 1984–1986. Nine of these discharged more than 100×10^6 l d^{-1}, and 24 discharged more than 20×10^6 l d^{-1} (Gunther *et al.*, 1987). Eighteen industrial discharges all release more than 400 000 l d^{-1} of waste to the bay, including six petroleum refineries that each discharge from 1–63 $\times 10^6$ l d^{-1} of waste. Selenium inputs from the petroleum refineries alone are comparable to riverine inputs at low flow (Cutter, 1987). In all, 200 permits have been granted for industrial waste releases (Luoma & Cloern, 1982). Nickel and selenium are discharged in the largest quantities from point sources relative to the riverine inputs (Table 1). Silver, mercury, cadmium and arsenic loadings are poorly quantified, however.

The point source trace element inputs are accompanied by inputs of untreated surface runoff (mostly from urban areas) from more than 50 small local streams. Few direct studies of the urban runoff are available (Gunther *et al.*, 1987), but estimates suggest loadings of Pb and Zn are the largest among the trace elements in this source (Table 1).

Other, smaller sources of trace element input also are common. Methylated tins, Cu and other contaminants are of concern around the more than 20 small boat marinas plus several large naval bases and commercial harbours that occur in the Bay. An estimated 6 millon m^3 of fine sediments are dredged annually from the harbours and marinas and these metal-enriched spoils are deposited at three sites in Central Bay and the northern reach of the estuary (Gunther *et al.*, 1987). Additionally, more than one spill of some hazardous material occurs every day within or on the shores of the Bay (Luoma & Cloern, 1982); forty sites of hazardous waste disposal on the shores of the bay are thought to be leaching into the estuary (Gunther *et al.*, 1987); a number of historic waste disposal sites within the bay retain their trace element contamination; and at least one abandoned mercury mine occurs on a local tributary.

The large mass of trace elements originating from the rivers suggest that these inputs establish background concentrations in the estuary upon which the effects of local anthropogenic inputs are superimposed. Even if contaminants from individual non-riverine inputs are only distributed locally at the point of discharge, however, literally hundreds of such areas of local concern could occur in San Francisco Bay.

Characteristics of trace element contamination

Temporal variability

Climatic and hydrologic driving forces can be highly variable on several different time scales in estuarine environments, and can affect trace element inputs, residence times and concentrations in the water column, sediments and biota. Variability caused by these natural processes must be separated from anthropogenic influences in any assessment of the latter.

Seasonal differences in trace element inputs from riverine sources are dramatic in San Francisco Bay. River flow and suspended sediment loads commonly are more than tenfold different between the high flow period of January–June and the low flow period from July–December (Conomos, 1979). Thus, each year a large input of particulates that are relatively uncontaminated with most trace elements is carried into the estuary in spring. A shift from dominance of trace element concentrations by riverine inputs during high flow to dominance of local influences during low flow is evident in the water column of the northern reach. Dissolved Cu (Eaton, 1979; Gordon, 1980) and dissolved total Se (Cutter, 1987) are distributed more conservatively during spring, at high river flows (declining approximately linearly with increasing salinity from the head to the mouth of the estuary) than during summer at lower flows. Local inputs from within the estuary are most evident in the head-to-mouth profiles of both elements at the lowest flows (Eaton, 1979; Cutter, 1987).

Distinct seasonal cycles of wind, freshwater input and tidal velocity in the Bay also cause seasonal variations in the characteristics of surface sediments that have implications for trace element concentrations.

A general seasonality in grain size distributions and associated parameters was clear in near-monthly data collected between 1977 and 1985 by Thomson-Becker & Luoma (1985). Sediments on intertidal mudflats were more coarse in summer when wind velocities were high. Finer grained materials were more dominant in autumn and winter when winds receded and as freshwater inputs of terrigenous particulates increased (Thomson-Becker & Luoma, 1985). In deeper waters tidal velocity also was important (Nichols & Thompson, 1985). Changes in grain size distribution were accompanied by changes in concentrations of organic material, Fe and Mn (Thomson-Becker & Luoma, 1985; Luoma *et al.*, 1988).

Trace element concentrations in surface sediments at shallow water or intertidal stations can fluctuate as much as ten-fold within a year, although a two to four-fold range of fluctuation is more common (Luoma *et al.*, 1988). The constantly changing character of the sediments may contribute to such variations. This influence is most evident where metal concentrations are lowest, and confounding anthropogenic inputs are least important. For example, concentrations of Cu correlated very strongly with total organic carbon ($r = 0.85$) in sediments collected near-monthly for three years from four intertidal stations with relatively low Cu concentrations (Luoma *et al.*, in prep.). Concentrations of Cu varied from 15 $\mu g\ g^{-1}$ to 60 $\mu g\ g^{-1}$ at one of these stations. However, nearly all that fluctuation followed organic carbon concentrations, and thus appeared to be driven by fluctuating sediment characteristics (Fig. 1a). The anthropogenic component of sediment contamination also fluctuates with time. Figure 1b shows the differences between Cu concentrations predicted from the above regression and concentrations observed at a station in San Pablo Bay. Copper contamination in

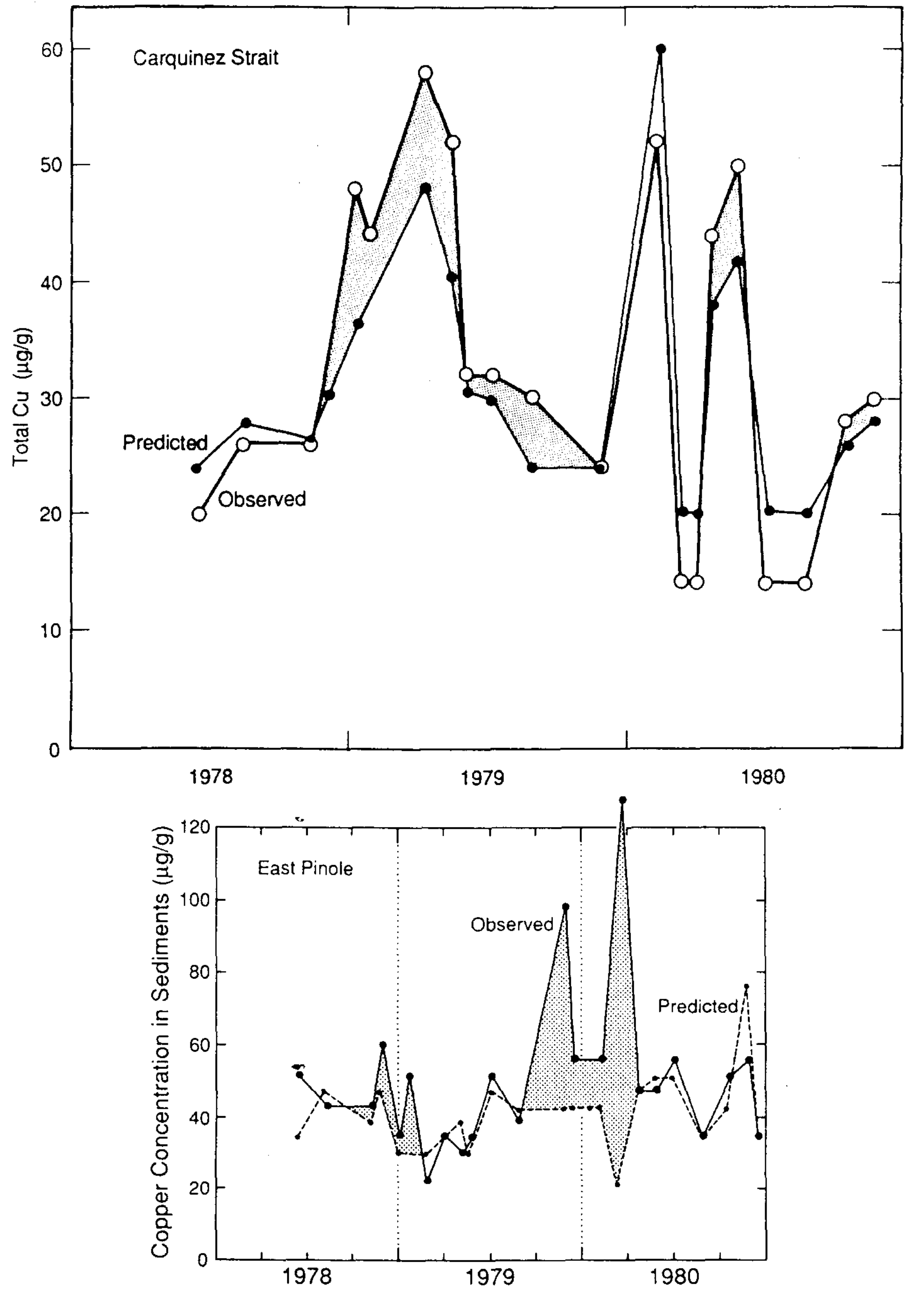

Fig. 1 *a.* Concentrations of Cu in sediments observed in 1978 through 1980 at a station in Carquinez Strait. Observed concentrations are compared to concentrations predicted from the regression of Cu and total organic carbon at stations with low Cu concentrations. *b.* Observed and predicted concentrations of Cu (as above) at a station in San Pablo Bay.

excess of that predicted from organic carbon concentrations occurred throughout one of the three years studied, but not in the other two. The occurrence of such transient periods of enrichment in the sediments of an urbanized estuary provides an additional challenge to the difficult task of monitoring in such environments.

Data on trace element concentrations in tissues of biota aid interpretations of the distribution of biologically available trace elements in estuaries. Such data also are subject to biases introduced by the complexities of the estuarine environment, however (Phillips, 1980; Bryan *et al.*, 1980, 1985). For example, seasonal and year-to-year fluctuations in growth promote fluctuation in tissue trace element concentrations within benthic species (Cain & Luoma, 1986; Cain *et al.*, 1987). The influence of size (or age) on trace element concentrations in estuarine animals also is well recognized (Boyden, 1974; Bryan & Uysal, 1978), and may influence comparisons of element concentrations among different populations of animals (Strong & Luoma, 1981; Cain *et al.*, 1987; Johns & Luoma, 1988). Fluctuations of biologically available concentrations of elements in water, sediment and/or food of organisms also occur (Cain & Luoma, 1986). The combined influences of biological and geochemical processes can cause trace element concentrations in benthic molluscs in San Francisco Bay to fluctuate as much as tenfold within a year. Concentrations are generally highest in November–April (Luoma *et al.*, 1985, 1988). The amplitude of the fluctuations also differs among stations and increases with enrichment, so that the most contaminated sites are the most difficult to study (Luoma *et al.*, 1985, 1988).

Spatial distribution of contamination

Trace element contamination in an estuary may be reflected in concentrations in the water column, sediments and biota. A few analytically reliable studies of trace elements in solution have been conducted in San Francisco Bay, although most such studies are restricted to the channels of the Bay (i.e the extensive shoal areas have been poorly studied). Numerous studies of sediments are available, but most of these fail to account for sediment characteristics that could affect trace element concentrations (e.g. particle size). Thus much of this work is of little value for spatial comparisons, especially where known areas of sandy and fine-grained sediments are compared (the importance of this effect was specifically demonstrated by Luoma *et al.*, 1988). A number of studies of trace element concentrations in benthic species also are available. However, no single sessile species occur throughout San Francisco Bay in sufficient abundance to be universally employed as a bioindicator. Thus, data on trace element concentrations in benthos in the bay are scattered among a variety of species (mostly molluscs), and include studies with both transplanted and resident animals. The comparable trace element data that are available from water column, sediments and/or biota support three generalizations concerning trace element distributions in San Francisco Bay: *1.* Concentrations of many elements are higher in the urbanized/industrialized portion of the estuary than in the rivers above the urbanization; *2.* Some elements are generally more enriched in South Bay than in the northern reach; and *3.* Distributions of most elements appear to be characterized by localities of extreme enrichment.

Element enrichment at the head of the urbanized estuary. The concentration of many trace elements increases at the head of San Francisco Bay where industrial and municipal waste discharges first appear (see Fig. 3, Wright & Phillips, this issue, for map). This suggests an important role for local sources in trace element contamination within the Bay. By sampling frequently to account for temporal variability, recent studies compared element concentrations in the lower San Joaquin River with concentrations at several stations within the urbanized estuary. Concentrations of As, Cd, Cr, Cu, and Se were highest in sediments and bivalves (*Corbicula* sp.) at stations within the influence of urbanization (Luoma *et al.*, 1988; Johns & Luoma, 1988). Lead and Zn were slightly elevated in Bay sediments, but not in *Corbicula.* Concentrations of Ag and Hg were similar in the Bay and the river. The results for Se were corroborated by determinations from the water column (Cutter, 1987). The river was an important source (relative to the estuary) of dissolved selenate during high flow in April, 1986, but not during lower flows in September 1985. However the highest concentrations of dissolved selenite and of suspended particulate-bound Se always occurred within the estuary (consistent with observations of Se in bivalve tissues — Johns & Luoma, 1988). High concentrations of selinite also were documented in effluents of refineries discharging near the point of enrichment in the Bay. Irrigation return flow causes Se contamination in the middle reaches of the San Joaquin River (Clifton & Gilliom, 1988), but that Se rarely seems to reach San Francisco Bay. Johns & Luoma (1988) suggested that was because of the substantial dilution and diversion of the San Joaquin River during most of the year, before it reaches the Bay.

Trace element distributions at the head of the Bay also may be affected by the physical processes in the estuary. Particle formation (Sholkovitz, 1976), or trace element desorption at the freshwater/seawater interface could be important; as might hydrodynamic processes such as tidal pumping (Ackroyd, 1987). During much of the year these processes would be most active in areas subjected to waste discharges. The possible effects of such interactions have not been investigated, however.

Enrichment in South Bay. South Bay is a large, semi-enclosed system with small freshwater inputs, mostly from sewage discharges at its southern terminus. Five of the eight largest waste treatment plants discharge their wastes into South Bay, which may partly explain the generally enriched concentrations of Cu, Cd, Se, and Ag that occur there.

The range in concentration of dissolved Cu, Se and Cd in solution is similar in South Bay as in the northern reach, (e.g. Cu 0.07–5.3 $\mu g\ l^{-1}$; total Se, 0.016–0.360 $\mu g\ l^{-1}$; Cd, 0.02–0.110 $\mu g\ l^{-1}$), but concentrations at equivalent salinities are higher by more than two-fold in

South Bay. Elevated Se concentrations also were observed at one site in South Bay in sediments, benthic organisms and birds (Johns & Luoma, 1988; Ohlendorf *et al.*, 1986). Localities of strong enrichment in sediment and biota are evident for Cu and Cd in South Bay (Luoma & Cloern, 1982; Luoma *et al.*, 1985), but a definition of regional enrichment awaits further study.

Geochemical processes may influence concentrations of dissolved Cu and Cd in South Bay. Concentrations of dissolved Se decline in a linear fashion through the small salinity range (20–35‰ in most studies) (Cutter, 1987). However, Cd and Cu show more complex distribution patterns in any individual profile (e.g Cu, Cd — Girvin *et al.*, 1978; Kuwabara *et al.*, 1988). Copper correlated strongly with concentrations of dissolved organic carbon in transects conducted over several seasons (Kuwabara *et al.*, 1988), suggesting complexation may play an important role in distribution of this element. Concentrations of dissolved Cd increased with suspended particulate material, especially near the terminus of South Bay. Either desorption was an important source of Cd or the source was coincident with the source of suspended particulate materials (Kuwabara *et al.*, 1988).

Evidence of Ag enrichment in both South Bay and Central Bay comes from studies with both sediments and biota. Concentrations of Ag found in the sediments of the northern reach of San Francisco Bay are typical of unenriched estuarine sediments (<0.5 μg g^{-1} dry wt; Peterson *et al.*, 1972; Luoma *et al.*, 1988). Sediments in South Bay contained 0.5–0.7 μg g^{-1} Ag in 1970 (Peterson *et al.*, 1972) and averaged 1.02 ± 0.18 μg g^{-1} at 22 stations in 1986 (Axtmann & Luoma, unpublished).

Silver is strongly accumulated by invertebrates in estuaries, and thus enrichment is much more evident in biological tissues than in sediments (Thomson *et al.*, 1984). Concentrations of Ag in benthos are typically low in the northern reach (Fig. 2). However, the extent of contamination of biota in South Bay and Central Bay led Phillips (1987) to conclude that Ag was an element of principal concern in San Francisco Bay. For example, one of the highest concentrations of Ag among the 110 reported by the national Mussel Watch programme in 1976–1978 was from the South San Francisco Bay station (Goldberg *et al.*, 1983). Concentrations in *Mytilus californianus* transplanted to the central part of South Bay through Central Bay in the 1980s were nearly all in the highest 15% of the 358 determinations made throughout California by the State Mussel Watch programme (Hayes & Phillips, 1987). The concentrations of 0.7–2.9 μg g^{-1} dry wt in *M. californianus* reported in 1982 (Fig. 2; Ladd *et al.*, 1984) in this area compared to 0.04–0.16 μg g^{-1} at reference stations.

The distribution of Ag in South and Central Bays also is quite heterogeneous. Relatively low concentrations are found in animals transplanted or collected from near the channel in the southern terminus of South Bay. However, concentrations at a nearby intertidal station (Palo Alto) in both the clam *Macoma balthica* and *M. californianus* are extremely high (e.g the values of 200 μg g^{-1} dry wt found in *M. balthica* are as high as any reported in the literature). Extreme Ag enrichment also was recorded in several other sloughs in both Central and South Bay (Thomson *et al.*, 1984; Hoffman & Meighan, 1984; Smith *et al.*, 1986; Chapman *et al.*, 1987). Available data suggests such extreme enrichment occurs only at the margins of the South and Central Bay, but that merely may reflect a lack of detailed study at deeper wastewater discharges. The area of most extreme Ag enrichment in sediments also is abiotic (inner Islais Creek — Chapman *et al.*, 1987), and measurements of tissue concentrations are therefore not available.

Localized Contamination. Studies to date firmly support a heterogeneous distribution of trace elements in San Francisco Bay, as typified by Ag (Fig. 2). The number of locally contaminated areas and the characteristics of their contamination are not well documented, nor is the relative extent of contaminated vs. less contaminated area in the Bay as a whole. Anthropogenic inputs appear to be the source of most localized areas of contamination.

A systematic picture of localized contamination is not available. Most studies are inconsistent in approach, of limited comparability, and are not spatially comprehensive. These problems are compounded by the size of the Bay, the number of possible trace element inputs and the physical/hydrologic complexity of the system. Nevertheless, localities of substantial contamination in either sediments or biota with Cu, Cd, Cr, Pb, Se, Hg, and methylated tins have been identified in all segments of the Bay (Girvin *et al.*, 1975; Luoma & Cloern, 1982; Hayes *et al.*, 1985; Luoma *et al.*, 1985; Hayes & Phillips, 1986; Stephenson *et al.*, 1986; Karras & Belliveau, 1987; Luomas *et al.*, 1988). Enrichment with As and Zn seems more rare.

The heterogeneous distribution of trace elements in San Francisco Bay is consistent with the large number of possible anthropogenic inputs. Indeed, patches of trace element contamination have been associated with inputs from sources such as municipal discharges, industrial discharges, and marinas or harbours. The extent of most individual patches is poorly known, however, and relationships between patch size and input are not established. Luoma & Cloern (1982) showed that Cu concentrations in *M. balthica* at six stations (each sampled several times over 3 yr) were correlated with Cu discharges from the nearest waste water treatment plants. Thomson *et al.*, (1984) defined a patch of Ag and Cu enrichment at Palo Alto, on the margin of South Bay, as extending south from the discharge of a local municipal sewage works for several kilometres. The enrichment was less evident north of the discharge. Tributyltin contamination appears to be most severe within harbours and marinas, in the few studies that have been conducted, but apparently does not extend far outside those localities (Goldberg, 1987; M. Stephenson, 1987). Concentrations of tributyltin in mussel tissues in several harbours in the Bay were among the highest found in California by the State Mussel Watch (Hayes & Phillips, 1987), but concentrations outside the harbours were considerably closer to those at reference stations (Table 2). Luoma *et al.*,

(1988) demonstrated strong Cr enrichment in *Corbicula* within the vicinity of the largest industrial discharger of Cr in the Bay. Concentrations in the bivalve fluctuated in coincidence with Cr discharge. In this case, the contamination appeared to extend throughout Suisun Bay.

Severity of Contamination

Although the studies that employed reliable analytical methodology are limited, trace element concentrations in solution in San Francisco Bay appear similar to those observed in other urbanized estuaries. The highest concentrations of Cu in solution, for example, are similar to maximum concentrations in anthropogenically influenced estuaries such as Narragansett Bay (Mill & Quinn, 1984), the Scheldt in the Netherlands (Valenta *et al.*, 1986; Van den Berg *et al.*, 1987) and Blanca Bay in Argentina (Villa & Pucci,

TABLE 2
Tributyltin concentrations in tissues of transplanted *Mytilus californianus* (data from Hayes & Phillips, 1987).

Location	Concentration TBT ($\mu g\ g^{-1}$ dry wt)
San Francisco Bay	
Pinole Point	0.066
Richmond Inner Harbor	0.97
Alameda Yacht Harbor	0.67
Oakland Inner Harbor	0.66
Southern California	
Los Angeles–Long Beach Harbor	0.52–0.72
Anaheim Bay	0.30–1.47
Newport Bay	1.55
Commercial Basin–San Diego Bay	1.56
Northern California	
Humboldt Bay	0.083
Pacific Ocean	
Bodega Head	<0.015

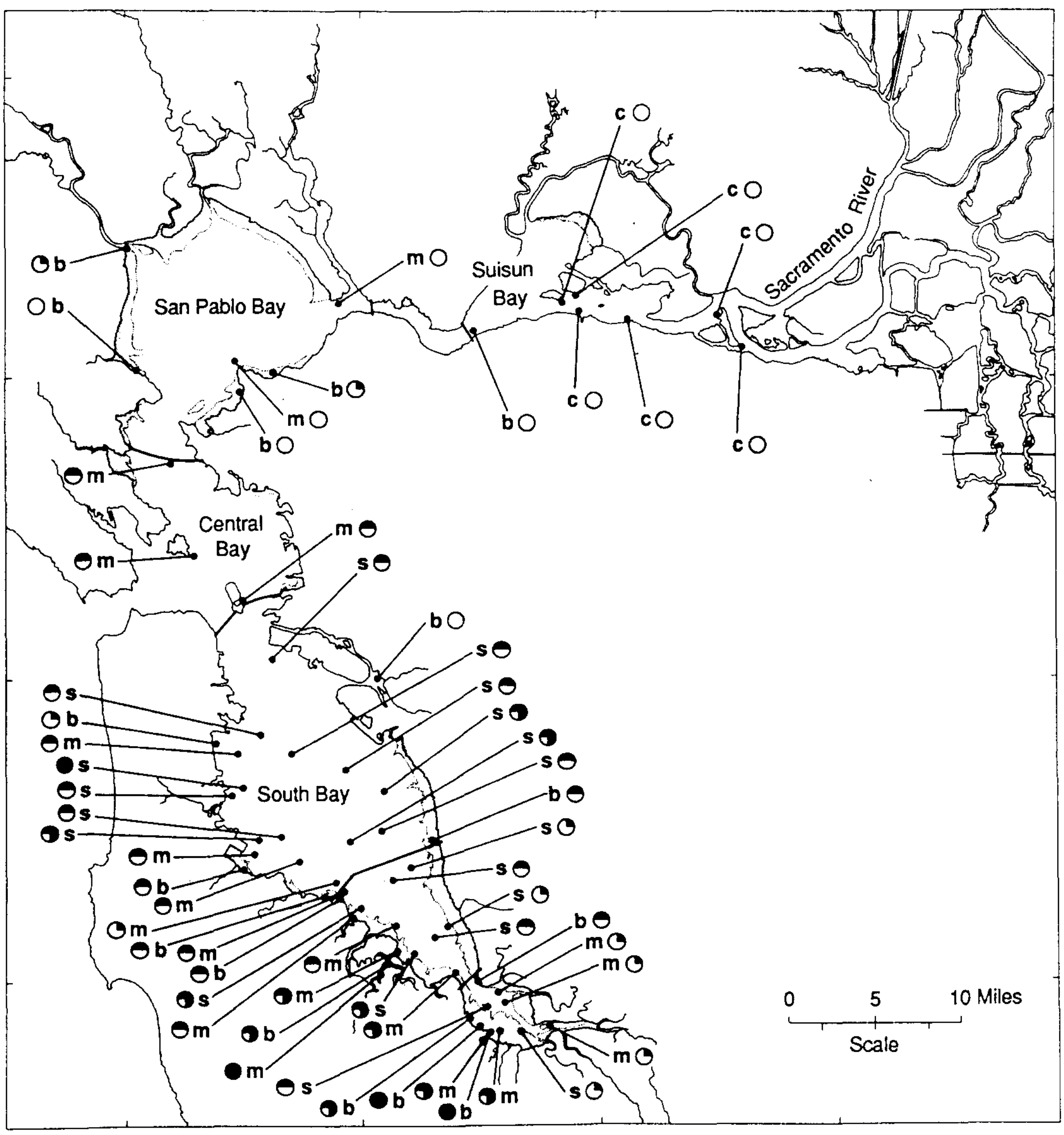

Fig. 2 Concentrations of Ag ($\mu g\ g^{-1}$ dry wt) in four species of bivalves collected in San Francisco Bay. m: transplanted *Mytilus californianus* collected in 1982 (Hayes *et al.*, 1985): b: *Macoma balthica* collected 1980 (Luoma *et al.*, 1986; unpublished data); c: *Corbicula sp.* collected 1983–1985 (Luoma *et al.*, 1988); s: *Musculista senhousia* collected 1986 (Carter & Luoma, unpublished data).

	○	◔	◓	◕	●
C.	<0.5				
M	0.05–0.2	0.3–0.7	0.7–1.5	1.5–4.0	>15.0
B	0.5–1.5	1.5–5.0	5.0–10	10–20	30–>100
S	<15	15–20	20–30	30–40	>40

1987). These concentrations are approximately twice higher than the maximum observed in undeveloped estuaries such as the Amazon (Boyle *et al.*, 1982) or the Brazos in Texas (Keeney-Kennicut & Presley, 1986).

Interpreting the severity of enrichment in sediments and animals requires recognition of the heterogeneity of trace element distributions. Early studies concluded that average trace metal enrichment in sediments Bay-wide was not severe compared to other systems (Bradford & Luoma, 1980). Indeed, times and places occur for each trace element in sediments and biota where concentrations do not exceed those at reference sites (See 'Mussel Watch' summary in Phillips, 1987 for the most comprehensive, comparable examples; Luoma, unpublished data). However, localities with trace element concentrations in both sediments and biota equal to the most enriched areas reported anywhere also are observed.

The elements that occur most frequently in concentrations exceptional for estuaries or marine environments are Ag, Cd, Pb, and perhaps Hg (e.g. Katz & Kaplan, 1981; Luoma & Cloern, 1982; Luoma *et al.*, 1988—Table 3). Extreme Cu enrichment in sediments (>300 μg g^{-1} dry wt.—Katz & Kaplan, 1981) is rare. However, high Cu concentrations in the tissues of benthic molluscs (mussels, clams, and snails), compared to what might be expected from sediment, are common (e.g. Fig. 3—Luoma, 1988). Concentrations of Cu in bivalves at several localities in South Bay and in the northern reach are as high as any reported, in areas where sediment enrichment seldom exceeds 100 μg g^{-1} (Luoma & Cain, 1979; Luoma *et al.,* 1988). This tendency toward biological enrichment led Luoma *et al.* (1985, 1988) to suggest that Cu might be unusually available to benthic biota in the Bay, perhaps because of some undefined geochemical characteristics of this environment (Luoma, 1983). If that is the case, the impacts of discharges containing Cu might be accentuated in this system.

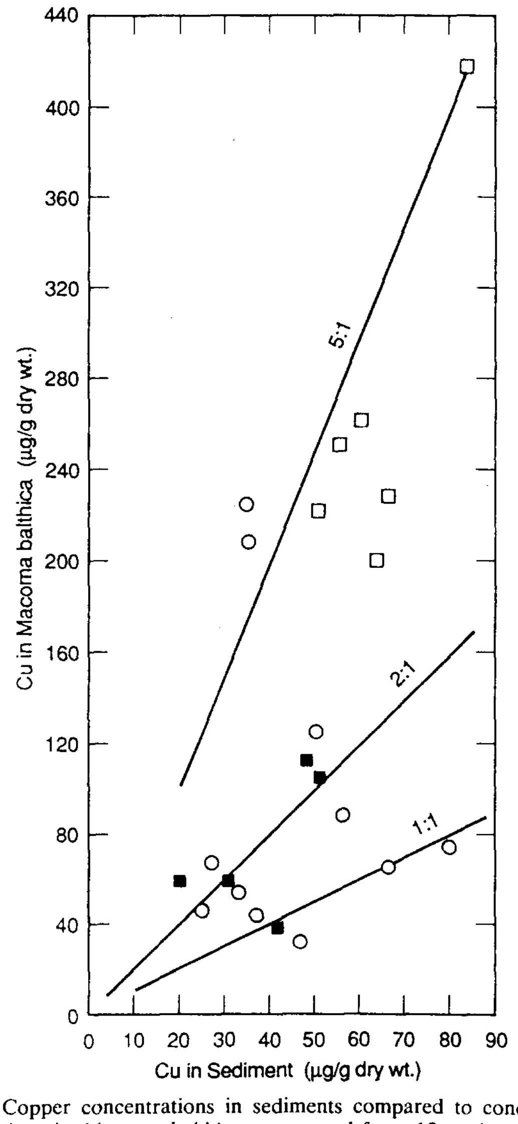

Fig. 3 Copper concentrations in sediments compared to concentrations in *Macoma balthica* as reported from 12 stations in the United Kingdom (Bryan *et al.*, 1980) and 7 stations in San Francisco Bay. Lines represent 5:1, 2:1 and 1:1 relationships between sediments and animals. O: English estuaries; □: Cu concentrations in winter in SF Bay; ■: Mean concentrations among 30 samples at five stations in SF Bay.

In contrast to Cu, the bioavailability of Pb may be reduced by geochemical processes in the Bay. Patches of strong Pb enrichment are common in sediments (Table 3), but not in benthic biota. For example, among 84 analyses of transplanted *M. californianus* in the State Mussel Watch studies, only 6 values exceeded those from reference areas by more than 3-fold (Hayes *et al.*, 1985; Hayes & Phillips, 1986; Stephenson *et al.*, 1986). Although the differences between sediments and animals may represent sampling bias, a reduced bioavailability of Pb is feasible given the relatively high concentrations of Fe typical of the Bay sediments, and the inhibitory effect of Fe on Pb bioavailability from sediments (Luoma & Bryan, 1978).

Long-term Changes in Trace Element Concentrations

Long-term changes in trace element concentrations in estuaries are typically difficult to evaluate. Historical data often do not exist, and the data available may be biased by changing analytical capabilities. The earliest data available for San Francisco Bay that employed adequate quality control are from the early to mid-1970s (Peterson *et al.*, 1972; Risebrough *et al.*, 1977; Girvin *et al.*, 1978). A number of similarities are apparent between these historic studies and recent data. Concentrations of Cu in solution (Girvin *et al.*, 1978; Kuwabara *et al.*, 1988) and in sediments (Peterson *et al.*, 1972; Axtmann & Luoma, unpublished) in South Bay agree remarkably well between studies separated by a decade or more (Fig. 4). The spatial distributions of Pb, Hg, and Zn in mussels appear similar among studies where comparisons are possible. Enrichment of Se near Carquinez Strait, evident in mussels in 1976 (Risebrough *et al.*, 1977), also was observed in clams in 1984–1986 (Johns & Luoma, 1988). A localized area of trace element contamination in Redwood Creek was reported in all studies between 1972 and the present (Girvin *et al.*, 1975; Risebrough *et al.*, 1977; Smith *et al.*, 1986).

Several differences among studies are also apparent.

1. Concentrations of Cd in solution in South Bay in 1985 (Kuwabara *et al.,* 1988) were twice as high as measured in 1976–77 (Girvin *et al.,* 1978) (Fig. 4). Localities of Cd enrichment also were observed in *Musculista senhousia*, between the San Mateo Bridge

TABLE 3
Trace element concentrations in sediments at 19 localities exhibiting trace element enrichment. Station order is south to north.

	Ag	Cd	Cr	Cu	Hg	Ni	Pb	Se	Zn
Coyote Creek		6.7	76	42	6.8	106	66	1.1	
Guadalupe Slough		3.7	67	37	5.4	89	52	0.9	170
Palo Alto	4.0			107					245
Hunters Point	2.0				0.4	130	54		202
Alameda Air Station		6.0	95		10.0	84	150	9.6	380
Oakland Inner Harbor					4.9	189	130		310
Oakland Outer Harbor		15.6	285			150			405
East Bay Municipal Outfall	4.0					100			170
Alcatraz Dredge Spoils	1.9	2.0			0.5	89	54		140
Islais Creek	13.0	10.0	740	130	6.9	190	1300		1200
Warmwater Cove	1.2		240			530	330		1400
China Basin	25	11.0	190	380	4.2	130	2900		
Point Isabel							704		553
Richmond Harbor					1.8	31			550
Sausalito		2.4			10.5		89		218
Hamilton AFB	22.5	6.1	76	50		99	375		
Mare Island Military Base	2.2	8.3		142	1.6	93	124		624
Concord NWS	66.0	10.2		128		343	2500	35	1890

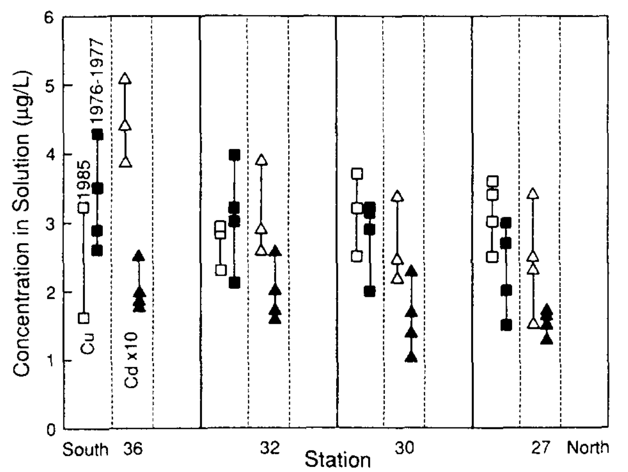

Fig. 4 Comparison of Cu, and Cd concentrations in solution observed at four stations in South San Francisco Bay in 1976–1977 (Girvin *et al.*, 1978) and 1985 (Kuwabara *et al.*, 1988).

and the Bay Bridge in 1986 (Carter & Luoma, unpublished) that were not evident in 1976 in analyses of *Mytilus edulis* from the same area (Risebrough *et al.*, 1977). The limited number of stations in both studies make comparison of such distributions quite speculative. Nevertheless, the possibility that Cd is increasing in concentration in South Bay is certainly worthy of further study.

2. Concentrations of Ag were all less than 0.7 $\mu g\ g^{-1}$ dry wt in 34 sediment samples from South Bay analysed by arc emission spectrography in 1970 (the mean of 30 samples where Ag was detectable was 0.56 $\mu g\ g^{-1}$) (Peterson *et al.*, 1972). In 22 sediment samples collected through the same area in 1986 (Axtmann & Luoma, unpublished) the mean Ag concentration was $1.02 \pm 0.16\ \mu g\ g^{-1}$, and only one sample had $<0.7\ \mu g\ g^{-1}$ Ag. The Ag enrichment apparent in Central Bay and lower South Bay in 1981–1987 in *M. californianus* and *M. senhousia* (Fig. 2) also was not apparent in *M. edulis* collected in 1976 from similar sites (Risebrough *et al.*, 1977).

Near-monthly data collected since 1975 from 1 km south of the Palo Alto wastewater treatment (Thomson *et al.*, 1984; Luoma *et al.*, 1985) offers an opportunity to assess changes in concentration at a metal-contaminated locality over the decade. Concentrations of Ag and Cu in sediments and benthic biota were enriched at this station throughout the study, and the sewage discharge was established as the predominant source of the metals (Thomson *et al.*, 1984). The enrichment increased between 1977 and 1979 (Luoma *et al.*, 1985; Fig. 5), as did the frequency of high metal loadings from the treatment facility (Thomson *et al.*, 1984). The waste treatment process at this plant was upgraded in late 1979, and in 1982–1983 Cu and Ag concentrations began to decline (Luoma *et al.*, 1985). In 1987 concentrations in sediments and biota were very similar to those observed at the onset of the study in 1975–1977 (Luoma *et al.*, 1985; Fig. 5).

The human population of the San Francisco Bay area has doubled since the early 1970s. The few comparable studies conducted during this period of growth suggest that the status of contamination in San Francisco Bay with metals such as Cu, Pb, Hg, and Zn has remained constant (probably because the continuing investment in waste treatment has kept pace with increased generation of such wastes). Waste treatment may not have been adequate to prevent increases in environmental concentrations of other metals, however (e.g. Cd and Ag). Furthermore, no clear decline in concentration of any trace element is evident in any reach of the Bay. No assessment is possible of whether the number of localized areas of contamination have changed. Systematic, comprehensive, comparable trace element monitoring programmes that extend for decades are essential if the understanding of progressive geochemical change in this estuary is to improve.

Biological impacts of trace element contamination

A complete understanding of the adverse impact of a pollutant in nature would require systematically showing that: *1.* unusual contaminant enrichment occurs in sediment or water; *2.* the contaminant enriched is biologically available; *3.* bioaccumulated contaminants are having adverse effects upon an organism at some functional level; *4.* functional (physiological) stress affects the well-being of the population; *5.* local changes in a population result in significant changes in the local biological community; and *6.* changes in local communities are of significance to the estuarine ecosystem as a whole.

The spatial and temporal characteristics of trace element enrichment in San Francisco Bay are the best understood of the six steps above. Some generalizations from work with a few species also are possible concerning the biological availability of the existing contamination. Few studies have considered the relevance of that information to entire food webs or upper trophic level species, however. Available data supports the suggestion that enrichment at a site in one benthic species commonly is accompanied by enrichment throughout a benthic community (Bryan & Hummerstone, 1978; Bryan *et al.*, 1980; Bryan & Gibbs, 1983; Bryan *et al.*, 1985). Differences among species in the capability for bioconcentration are well established. But similar differences in Ag contamination among five stations in San Francisco Bay were evident in six different benthic species (Table 4). Extension of existing trace element contamination to higher trophic levels also is indicated. The Cu and Ag enrichment observed in bivalves at Palo Alto and Redwood Creek is reflected in the high concentrations observed in liver and kidney tissues of local populations of diving ducks (Ohlendorf *et al.*, 1986). The same is true of the Se enrichment observed in Suisun Bay and Carquinez Strait (Ohlendorf *et al.*, 1987). In general, however, trace element contamination in upper trophic level species is not well studied in San Francisco Bay, or in any estuary.

Only a few studies have attempted to define whether trace element contamination causes physiological stress in species in San Francisco Bay, and whether that stress is translated into ecological change. In three studies the occurrence of stress in bioassays of whole organisms correlated with the occurrence of trace element enrichment, but covariance with other potential stressors also was present. Martin *et al.*, (1984) found that 'scope for

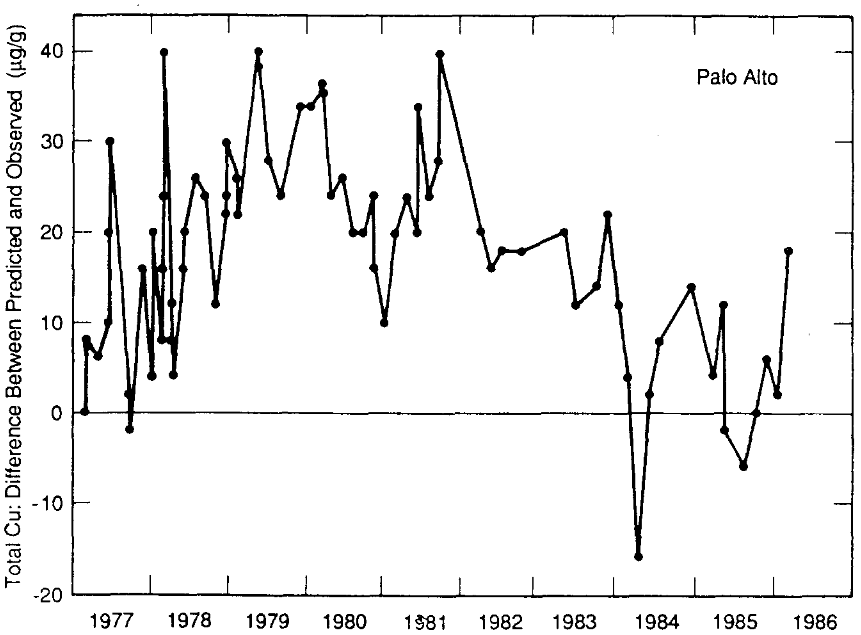

Fig. 5 The trend through time (1977–1986) of Cu contamination in sediments at Palo Alto. Contamination is defined as the difference between observed Cu concentrations in sediments and concentrations predicted from the regression of Cu and organic carbon at stations with low Cu concentrations. The difference represents Cu contamination after fluctuations driven by changes in the sediments are removed.

TABLE 4

Silver concentrations in six species from five intertidal stations in South San Francisco Bay. Order of enrichment of stations in each species (where data available) is: Coastal < Candlestick < Foster City < Redwood Creek < Palo Alto.

	Coastal Harbor	Candlestick Point	Foster City	Redwood City	Palo Alto
Tapes japonica (filter feeder)	0.7 ± 0.7	2.5 ± 1.1	9.7 ± 4.5	65	
Ilyanassa obsoleta (snail-grazer)		46 ± 1		176 ± 82	320 ± 160
Mya arenaria (filter feeder)		3.2 ± 0.8			34
Macoma nasuta (deposit feeder)		2.1 ± 0.7	5.1 ± 1.8		
Marphysa sanguinea (polychaete)			2.4 ± 0.5	5.5 ± 0.7	
Macoma balthica (deposit feeder)	1.2 ± 0.4	3.3 ± 1.6	6.2 ± 2.0	10.7 ± 0.7	67 ± 12

growth' in suspended mussels declined from the mouth to the terminus of South Bay, in coincidence with a number of variables, including increasing concentrations of trace metals such as Ag. Chapman *et al.*, (1987) demonstrated the toxicity of sediments from Islais Creek (a slough receiving waste water discharges in Central Bay) in bioassays with four different species. The sediments were severely enriched with trace elements, but also with trace organics and probably sulphides. Baumgartner *et al.* (unpublished EPA-USGS joint study) found surprisingly high mortality, compared to previous studies in other estuaries, in amphipod bioassays of oxic sediments conducted at 26 subtidal stations in South Bay. Seven stations had $\geqslant 50\%$ mortality in the bioassays. Where they were analysed, EPA priority organic pollutants were not exceptionally enriched at these seven stations, but the tissues of resident *Musculista senhousia* were among the most enriched with Ag, Cd, and/or Cu relative to the other stations in South Bay.

Of the above studies, only that of Chapman *et al.*, (1987) considered coincident ecological change. Although the ecological study was very superficial (they sampled only once and did not identify the date of sampling) gross ecological differences were evident where contamination was most extreme (inner Islais Creek). This is also an area where extreme salinity changes can occur aperiodically, however. Given the insensitivity of the approach it was not surprising that bioassay results and ecological studies were neither consistent nor conclusive at two other sites in the Bay where contamination was less extreme. Defaunated or extremely impoverished benthic communities also are found at other extremely contaminated/anoxic localities subject to drastic salinity changes (e.g. Mission Creek; Hoffman & Meighan, 1984) but accompanying toxicological or physiological studies have not been conducted.

Chemical characteristics of contamination, physiological stress and ecological change have been more thoroughly addressed at the metal contaminated site at Palo Alto. This site has no chronic anoxia problems; salinity fluctuations are typical of South Bay in general; and it is not in a slough. Thus it may be more typical of contaminated intertidal habitat.

Metal stress is indicated at Palo Alto at several levels of biological organization.

1. Sub-cellular. Johansson *et al.*, (1986) demonstrated a shift in the intracellular protein distribution of Cu and Ag in *Macoma balthica* during a period when metal concentrations were highest. Studies elsewhere indicate that similar changes in the intracellular distribution of Cu coincide with the onset of stress (i.e a reduction of growth) in crab larvae (Sanders & Jenkins, 1984). Coincident stress studies with *M. balthica* have not been conducted.

2. Whole organism. Production of biomass by *M. balthica* was lower during the increase in Ag and Cu enrichment that occurred in 1977–1979 than at any time between 1974 and 1981 at Palo Alto (Nichols & Thompson, 1985). In fact, the population disappeared in spring 1978, when contamination with both metals was most severe. This was one of two times in 14 years of study that *M. balthica* and a competitor on the mudflat, *Amplesca abdita*, simultaneously declined in abundance (Nichols & Thompson, 1985).

3. Population. M. balthica began to increase in abundance in 1979, resuming its apparent ecological competition with *A. abdita* (Nichols & Thompson, 1985), although metal enrichment did not decline until 1982 (Luoma *et al.*, 1985). However, the individuals comprising the *M. balthica* population in 1980 were 6 times more tolerant to Cu and Ag than individuals from adjacent populations in the Bay (Luoma *et al.*, 1983) and responded differently to metal inputs than individuals from other populations transplanted to Palo Alto (Cain & Luoma, 1985). Thus, reappearance of *M. balthica* in 1979 may have necessitated physiological adaptation or selection for a genetically metal-tolerant sub-population (Luoma *et al.*, 1983).

4. Absence of other species — whole organism bioassay. Selection or adaptation in one species implies a reduction in the survival of intolerant or inflexible individuals at the metal enriched site, and might signify difficulties for species less flexible than *M. balthica* (Luoma, 1977). The possibility of limited survival of potential colonizing species was partly addressed by a recent oyster bioassay study. Smith *et al.*, (1987) showed that 'chambering' is a specific growth deformity in juvenile oysters associated with the toxicity of tributyltin. Stephenson (1987) recently reported chambering in oysters transplanted to a number of marinas and harbours in the Bay. At Palo Alto, however, they found growth retardation of the oysters, but no chambering, perhaps a result of the metal stress indicated in the previous studies of *M. balthica*.

5. Community ecology. Despite the indications of stress at other levels of biological organization, ecological interactions that might be indicative of stress at Palo Alto are difficult to identify relative to natural variability. Variability in species abundance, with fluctuating dominance of different species, is typical of estuarine benthic communities. For example, the competitive fluctuation of *M. balthica* and *A. abdita* that occurs at Palo Alto also has been observed elsewhere (Nichols & Thompson, 1985). Furthermore the community at Palo Alto does not appear *superficially* different from communities at nearby less contaminated mudflats (although experience dictates that superficial observations are often misleading — Nichols, 1979). Clearly, life history studies of *M. balthica* and *A. abdita*, assessments of any role metals might play in the interspecies competition, or larval settlement studies of important species at Palo Alto and comparable environments are in order. In general, developing a better understanding of processes and changes that occur in undisturbed communities also will be an important part of defining the degree of metal-induced ecological disturbance at Palo Alto.

The studies at Palo Alto demonstrate the challenges of demonstrating the influences of trace elements on benthic communities. The critical levels of biological organization at which to assess stress have not been convincingly demonstrated; and controlling processes at some levels of organization, such as community ecology, are understood only crudely (Nichols & Thompson, 1985). Thus, at present, determining whether significant disturbance occurs at contaminant enriched localities depends upon systematic studies at several levels of biological organization, coordinated with geochemical studies of temporal and spatial characteristics of the contamination.

Defining the significance of trace elements in changes occurring at the ecosystem level is more problematic than defining disturbance at individual sites. Frequent disturbance appears to play a pronounced role in determining the generally patchy distributions of benthic species in San Francisco Bay (Nichols & Thompson, 1985). Periodic or spatially localized trace element contamination could be one form of such disturbance. The extent to which contamination represents disturbance, and the frequency or severity of such disturbances are not yet established for San Francisco Bay. If any ultimate system-wide impacts of trace elements in this estuary depend upon the aggregate effects of many small disturbances, establishing cause and effect will be particularly challenging.

Conclusions

Progress in recent years towards understanding the distributions and abundance of trace elements in San Francisco Bay suggest:

1. On the basis of loadings from anthropogenic sources, and frequency or severity of contamination in the water column, sediments, and biota, the elements of greatest concern are Ag, Cu, Cd, Se, and perhaps Hg. Nickel has not been studied. Elements of less concern are Zn and As. Copper appears to be of exceptionally high bioavailability in the bay; and Pb may be of low bioavailability.

2. The distribution of trace element contamination is complex in space and time, in coincidence with the large number and the diversity of anthropogenic sources of input. Localities of minimal trace element enrichment occur; as do localities of extreme enrichment. A systematic understanding of the details of this spatial mosaic of contamination awaits further study.

3. The limited available evidence indicates that trace element enrichment has changed little since the earliest studies in the 1970s; although Ag and Cd concentrations in South Bay may have increased. Changes in the number of patches of localized contamination, or the severity of contamination within such patches cannot be evaluated from existing data.

4. Stress in benthic communities is evident in extremely contaminated localities. Metal-induced stress on one benthic species is suggested by converging lines of evidence at a Cu–Ag enriched locality in South Bay. In general, however, studies to date have lacked the systematic approach, comprehensive nature and continuity of support necessary to establish rigorous scientific proof of trace element impacts on species in the Bay. There is a particular dearth of knowledge about upper trophic level species.

5. Frequent disturbance in space and time appears to play a major role shaping the structure and composition of the benthic community of the Bay. The patchy nature of trace element distributions suggests that they might provide one source of such disturbance, but knowledge of natural variability is too crude to be sure. If the ultimate system-wide impacts of trace elements partly depend upon the aggregate effects of many small disturbances, establishing cause and effect will be particularly challenging.

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Distribution of Trace Metals in the Sediments and Biota of Chesapeake Bay

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Trace metal distribution in Chesapeake Bay is dominated by the input from the Susquehanna River, although other inputs include shore erosion, industry, atmospheric deposition (especially for lead and zinc), and municipal wastewater. By most recent estimates the largest point source of metals, Baltimore Harbor contributes little to the main bay and there is only minimal transport of metals out of the northern bay.

Although Baltimore Harbor and the Hampton Roads complex account for most of the industrial metal output, particular concern is shown for metal contamination of spawning rivers, with cadmium, copper and aluminium (plus acid) implicated to some degree.

In general, studies of the effect of metals on biota are less advanced than in San Francisco Bay.

Although Chesapeake Bay oysters show high levels of trace metals compared with most other coastal areas of the US, studies of the effect of metals on biota are less advanced than in San Francisco Bay.

The estuarine environment is the last area for the removal of trace metals before their passage from the terrestrial to the marine environment. According to Turekian (1977) estuarine sediments are metal repositories and only a minor fraction of materials escapes to coastal waters. Biggs & Howell (1984) have estimated the trapping efficiency of suspended material in the Chesapeake Bay at 98±3%, which makes the Bay an efficient trap especially compared to the 61±12% for San Francisco Bay. Bottom sediments are long-term integrators of geochemical processes, hence information from sediments can establish the long-term behaviour of trace metals in estuaries. Since landings of freshwater-spawning fish and oyster harvests have decreased in recent years (Tippie, 1984), it is important to assess the effects of trace metals on various organisms. This paper reviews the distribution of trace metals in the sediments and the biota of Chesapeake Bay. Since trace metals have natural as well as anthropogenic sources, we identify contaminated areas and examine their influence on the bay as a whole.

The sediments in the bay show a decrease in grainsize from the Susquehanna River mouth to Kent Island (75 km from mouth) (Hennessee *et al.*, 1986). The fine-grained, metal-rich sediment brought into the bay by the Susquehanna River is predominantly deposited north of Baltimore Harbor (Schubel, 1968; Officer *et al.*, 1984). Located on the bay are two major industrial ports, the largest being Baltimore Harbor on the Patapsco subestuary in Maryland and the other the Hampton Roads area near Norfolk, Virginia.

A major geochemical survey of Chesapeake Bay sediments has included the spatial distribution (Sinex, 1981; Sinex & Helz, 1981) and temporal variations (Cantillo, 1982; Helz *et al.*, 1986) of trace metals. A number of general features are displayed by the data. In the surficial distribution, all metals show a decrease in concentration in the seaward direction. This trend reflects the declining influence of the Susquehanna River in the seaward direction. The Susquehanna, with