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Abstract Significant contamination of the tellenid clam *Macoma balthica* with Cu and Ag was observed at stations in southern San Francisco Bay. The degree of contamination appeared to be greatly influenced by the discharge of fresh water into South Bay. Local runoff appeared to provide an important source of the contaminants, especially in the summer and fall. Fresh-water discharge, either from local sources or from the Sacramento-San Joaquin Delta, also provided the force that flushed biologically available Cu and Ag from South Bay, and the degree of this flushing force appeared to determine the magnitude of the annual peak in Cu and Ag concentrations of the clam. A metal discharge index, combining an indirect estimate of annual metal loading (derived from cumulative rainfall) with the inverse of fresh-water discharge at the Delta, was found to explain 60-80% of the temporal variance in the Ag and Cu concentrations of *M. balthica*. The index represents a first step toward quantitatively predicting the effect of any reduction in fresh-water discharge into the Bay on Ag and Cu contamination in South Bay. Significant differences between temporal variations in Zn concentrations in the clams and the variations in Cu and Ag concentrations suggest all contaminants do not behave similarly in South Bay.



FLUCTUATIONS OF COPPER, ZINC, AND SILVER IN TELLENID CLAMS AS RELATED TO FRESHWATER DISCHARGE—SOUTH SAN FRANCISCO BAY

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Significant contamination of the tellenid clam *Macoma balthica* with Cu and Ag was observed at stations in southern San Francisco Bay. The degree of contamination appeared to be greatly influenced by the discharge of fresh water into South Bay. Local runoff appeared to provide an important source of the contaminants, especially in the summer and fall. Fresh-water discharge, either from local sources or from the Sacramento-San Joaquin Delta, also provided the force that flushed biologically available Cu and Ag from South Bay, and the degree of this flushing force appeared to determine the magnitude of the annual peak in Cu and Ag concentrations of the clam. A metal discharge index, combining an indirect estimate of annual metal loading (derived from cumulative rainfall) with the inverse of fresh-water discharge at the Delta, was found to explain 60-80% of the temporal variance in the Ag and Cu concentrations of *M. balthica*. The index represents a first step toward quantitatively predicting the effect of any reduction in fresh-water discharge into the Bay on Ag and Cu contamination in South Bay. Significant differences between temporal variations in Zn concentrations in the clams and the variations in Cu and Ag concentrations suggest all contaminants do not behave similarly in South Bay.

Trace metal contamination is often associated with the type of industrial/urban development which surrounds San Francisco Bay. South San Francisco Bay may be especially vulnerable to trace contaminant effects because the residence times of South Bay waters are long during most of the year. McCulloch et al. (1970), Imberger et al. (1977) and Conomos (1979) suggest that South Bay is well flushed only during periods of high fresh-water discharge from the Sacramento-San Joaquin Delta. Girvin et al. (1975) suggest that pollutants may accumulate in South Bay waters, sediments, and biota during periods of restricted flushing.

The discharge of fresh water into South Bay may affect the concentration of trace metals available to organisms in several ways: (1) River, stream and sewer discharge may carry elevated concentrations of solute and particulate-bound metals into the estuary during the rainy season. Urban storm runoff is characterized by high concentrations of many trace metals (Pitt and Amy 1973). (2) Terrigenous (land-derived) sediments are carried into the estuary primarily during the winter (Conomos and Peterson 1977). The physicochemical characteristics of the terrigenous sediments (especially those in urban runoff) may differ from the characteristics of the estuarine sediments. These differences may affect both the partitioning of metals between particulates and solution and the ability of organisms which ingest particulates to accumulate metals (Luoma and Jenne 1977; Luoma 1977a). (3) The facilitation of flushing by fresh-water discharge into South Bay may reduce concentrations of solute trace metals which accumulated in the water and/or change the chemistry of the sediments (again, affecting the availability of the metals to organisms) and (4) decreases in salinity of ambient waters, associated with fresh-water influx, may directly affect metal uptake by organisms (Phillips 1977a).

Any or all of the above effects should be reflected in temporal changes in the metal

SAN FRANCISCO BAY

concentrations of organisms in South Bay. Temporal variability in the metal concentrations in bivalves (Anderlini et al. 1975) and seston (Flegal 1977) were reported in North San Francisco Bay, but the causes of the variation were not discussed. Careful analyses of the causes of such variability have been useful in studying biological, physical and chemical influences on metal cycling in other estuaries (Luoma 1977a; Frazier 1975). In this chapter we present data from South San Francisco Bay on temporal changes in the concentration of silver (Ag), copper (Cu) and zinc (Zn) in the soft tissues of the tellinid clam *Macoma balthica*. The data extend from March 1975 to February 1978 and include a 2-yr period of severe drought, which significantly affected physical and chemical processes relevant to San Francisco Bay. We show that increases in fresh-water discharge enhance the biologically available concentrations of all three metals in South Bay, but also appear to modulate the removal of Cu and Ag from the estuary.

Macoma balthica was chosen for study because it is a deposit feeder (ingests sediment and associated organic matter for food), it concentrates a number of metals to a greater extent than the two other clams (*Tapes japonica* and *Mya arenaria*) common in South Bay (Luoma unpublished data) and it is widespread on intertidal mudflats throughout the Bay (see also Nichols 1979 and Carlton 1979). Silver (Ag), Cu and Zn were chosen because all are potentially toxic to estuarine organisms and are potentially important contaminants in South Bay.

Methods and Materials

Clams and sediments were collected at eight intertidal stations and one subtidal station in South Bay (Fig. 1). Our discussion will focus primarily on two of these stations (1 and 5) which have been sampled periodically since early 1975. Sediments were scraped from the surface oxidized layer, sieved through 250 μ m polyethylene mesh and extracted within 24 h of collection with either hydroxylamine hydrochloride in 0.01N nitric acid, 25% acetic acid, 0.1N sodium hydroxide or a mixture of concentrated nitric and sulfuric acids (for "total" metal). Specific extraction methodology is described elsewhere (Luoma in press).

The sediment extractions were used to assess the effects of fresh-water discharge on sediment chemistry, and to identify periods of terrigenous sediment movement in South Bay. Sodium hydroxide extractions were used to estimate the concentration of humic materials in the sediments. Humic acid concentrations in the extract were measured by absorbance at 480 nm. Humic materials originate primarily from bacterial metabolites in terrestrial soils and occur at higher concentrations when terrigenous input into sediments increases (Luoma and Bryan unpublished data). Hydroxylamine and acetic acid extractions were used to estimate the proportion of freshly precipitated iron in the sediments. In oxidized sediments, Fe occurs as a hydrated oxide primarily associated with the surface of particles (Jenne 1968, 1977). Iron oxides are highly amorphous when they precipitate but gradually become more crystalline with age. The solubility of Fe in hydroxylamine hydrochloride declines more rapidly as iron oxides age (crystallize) than does the solubility of Fe in acetic acid (Luoma in press). Thus, the ratio of Fe extracted from sediments by hydroxylamine relative to that extracted by acetic acid is an index of the proportion of freshly formed iron oxide. Freshly formed iron oxide enters the estuary and its tributaries primarily during periods of high runoff (Elder et al. 1976; Tefrey and Presley 1976). When terrigenous input of Fe is low, the oxides should increase in crystallinity as they age or mix with the "older" Fe in marine sediments. These seasonal changes should be reflected in the relative extraction of Fe by the two extractants.

Fifteen to 30 clams were collected at each sampling. The animals were kept for 24 h after collection in clean seawater to clear their gut of undigested sediments. Soft tissues were dissected from the shells, weighed, digested in a mixture of concentrated nitric and sulfuric acids (2:1, with the addition of excess HNO₃ where necessary), then evaporated to dryness and reconstituted in

LUOMA AND CAIN: TRACE METAL CONTAMINATION

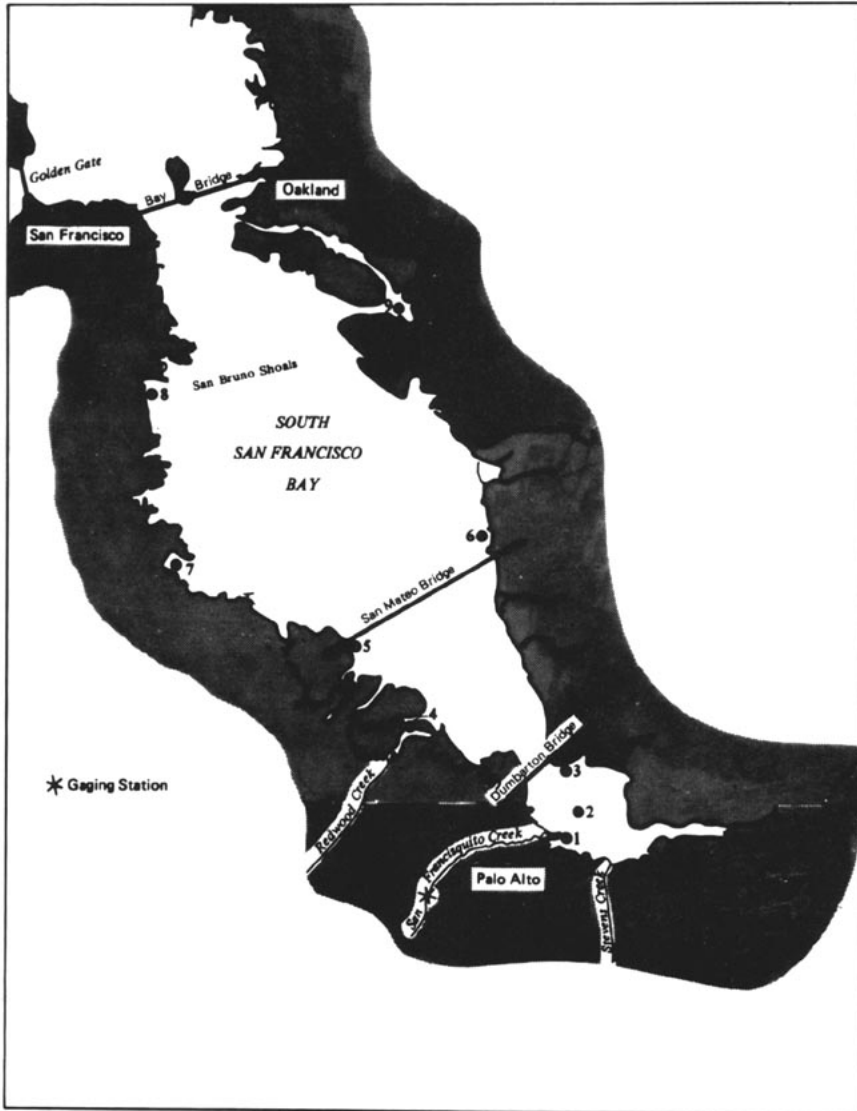


Fig. 1. Sampling stations in South San Francisco Bay.

25% HCl. (Reconstitution in HCl was essential to prevent precipitation of Ag in the samples). Analyses were conducted on either samples of pooled animals (in 1975 and early 1976) or on the tissues of individual animals by atomic absorption spectrophotometry with background correction where necessary. In a few instances significant correlations between metal concentration and the weight of individual animals were observed. Metal concentrations calculated for a median-sized animal (100 mg) from the regression equation for the concentration-weight relationship were used instead of mean concentration in all such samples.

River flow data were obtained from calculations of a Sacramento River-San Joaquin Delta

SAN FRANCISCO BAY

Outflow Index (see Arthur and Ball 1979); stream flow data were from the U. S. Geological Survey (USGS) gauging station on San Francisquito Creek (Fig. 1); and rainfall data were from National Weather Service data for Palo Alto. Estuarine water salinities were determined with a salinometer from shallow pools on the surface of the mudflats.

RESULTS

Physical and Chemical Environment

Physical variables. Delta discharge provides the major source of fresh-water influx into the entire San Francisco Bay system (Conomos 1979). San Bruno shoals and the narrows at the Dumbarton Bridge may impede the penetration of this Delta water into the southern reaches of the Bay (Imberger et al. 1977). Thus, local streams and sewers may be a very important source of fresh water in South Bay despite their relatively low rates of discharge. Local stream discharge was highly irregular during our study, closely reflecting the pattern of local rainfall (Fig. 2). Discharge from most local streams was negligible during the drought summers of 1976 and 1977. The discharge of the Sacramento River also declined substantially as the drought progressed (Fig. 2).

Chemical variables. Salinities at stations 1 and 5 were lower in the spring and winter of both drought years than in the summer, reflecting some significant seasonal increase in fresh-water inflow in South Bay despite the drought (Figs. 3, 4). Local stream discharge appeared to be a significant source of this fresh water. The minimum salinities observed at station 1 in 1976 (late March), and in 1977 (January, April, November) all followed the largest pulses of discharge from San Francisquito Creek observed in those years. Reduced salinities at station 5 in March 1976, and April 1977 also followed large pulses of stream discharge. The minimum salinity observed at station 5 (5 May 1977), however, was preceded by more than 30 days of relatively low stream discharge, suggesting Delta discharge may have penetrated to station 5 in May 1977. A surprising salinity minimum occurred in late August 1977 at stations throughout the South Bay (1, 3, 5, 6, 7, 8). This followed 90 days of no rainfall and zero discharge from all local streams (USGS Data Report in preparation; Santa Clara Valley Water District unpublished data) and coincided with a period of very low Delta discharge.

The humic acid concentrations measured in 1977-78 indicated little terrigenous input of sediment at station 5 until November (following the second storm of the year, but the first pulse of stream runoff measured at the USGS gauging station) and at station 1 until January (Figs. 3, 4). The proportion of fresh iron oxide in the sediments at station 5 followed the expected seasonal pattern with minor peaks following the large pulse of stream discharge in April 1977 and the first storm of the fall in September 1977 (Fig. 4). The proportion of freshly precipitated iron oxide at station 1 was consistently higher and less variable than at station 5 (Fig. 3). This is consistent with the strong influence of a high, relatively constant input of sewage into the southernmost reach (Imberger et al. 1977). Peaks in the proportion of fresh iron oxide in April 1976 and in February and April 1977, following the largest stream discharges of those years, suggested runoff also contributed Fe to the sediments at station 1. The winter maximum and the end of the summer minimum in the proportion of fresh iron oxide occurred earlier at station 5 than at station 1 in both years, as did the beginning of the winter increase in humic acid concentration. At both stations the anomalous salinity minimum in August 1977 was accompanied by a small increase in the proportion of fresh iron oxide, and the winter increase in humic acid concentrations preceded the increase in fresh iron.

Trace metal concentrations. To facilitate a meaningful perspective, the concentrations of Cu,

LUOMA AND CAIN: TRACE METAL CONTAMINATION

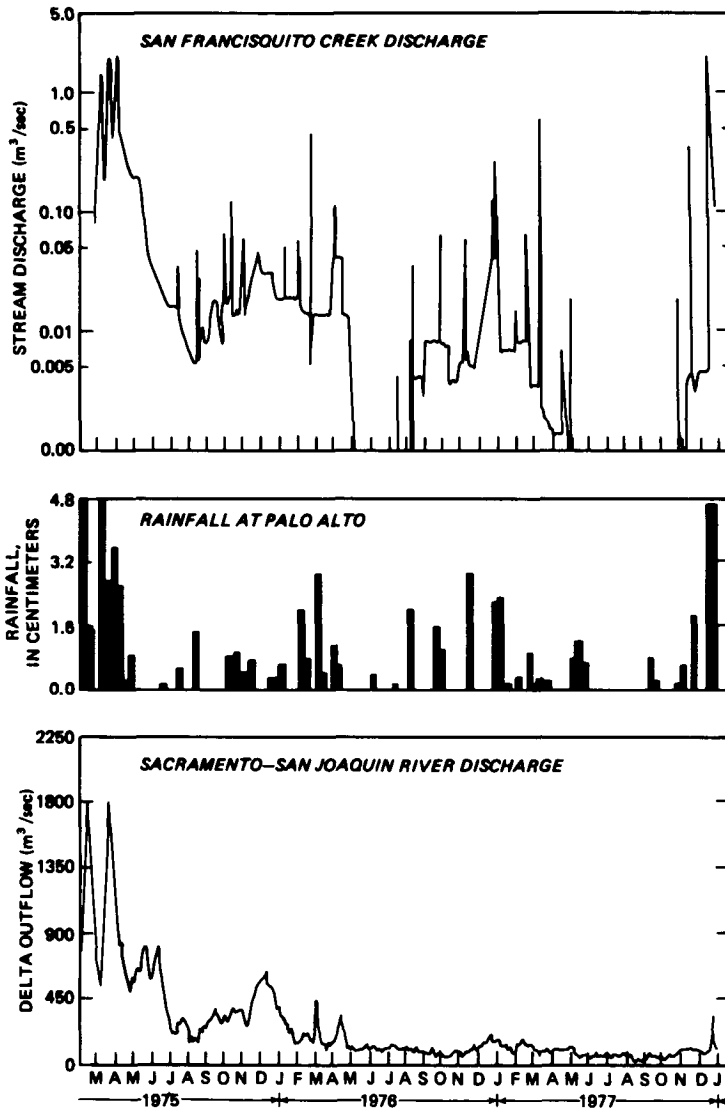


Fig. 2. Rainfall at Palo Alto (near station 1), fresh-water discharge from San Francisquito Creek (near station 1), and fresh-water discharge through the Sacramento-San Joaquin Delta between February 1975, and January, 1978.

Ag and Zn observed in South Bay sediments and clams (Table 1) were compared to similar observations from 17 English estuaries which ranged from pristine in nature to some of the most polluted estuaries in the world (Luoma and Bryan unpublished data). The tellenid clam *Scrobicularia plana*, from the English estuaries, is ecologically, morphologically and behaviorally quite similar to *M. balthica*. Where the two species co-occur in England their Ag, Cu and Zn concentrations are comparable (Bryan and Hummerstone 1977). Median Ag concentrations in clams from station 1 were nearly 100 times greater than concentrations in clams from more pristine environments (Table 1). Moreover, Ag enrichment in both sediments and animals was as great at station 1 in South Bay

SAN FRANCISCO BAY

as in any estuary in the English survey (Fig. 5) which included several estuaries with silver mines in their drainage basin. The Ag enrichment appeared to originate from a point source near station 1 on the western shoal, below Dumbarton Bridge, and was rapidly diluted north and east of station 1 (Table 1).

The concentrations of Cu and Zn in South Bay sediments were low relative to concentrations observed in metalliferous, or industrially enriched areas (Fig. 5; Table 1). Concentrations of

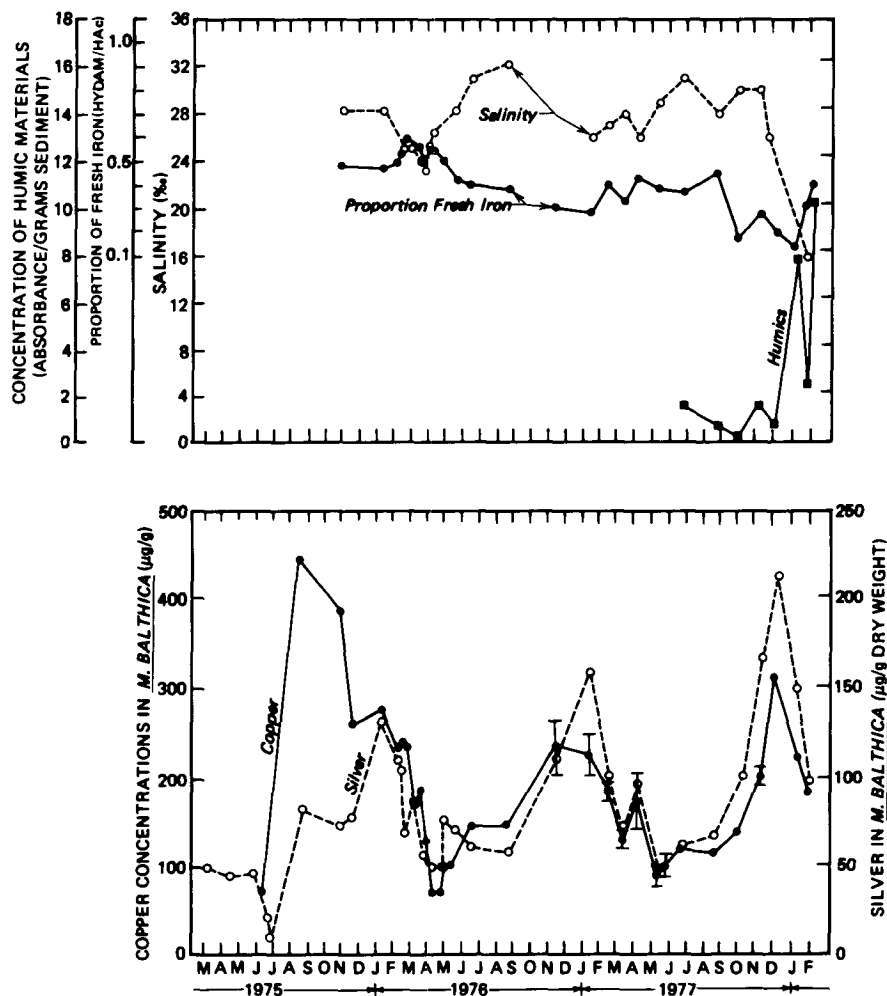


Fig. 3. Salinity, the proportion of freshly precipitated iron oxide in sediments, humic acid concentrations in sediments, and concentrations of copper (Cu) and silver (Ag) in *Macoma balthica* observed at station 1 between March 1975, and February 1978.

Zn in *Macoma balthica* were also low for this family of bivalves (Fig. 5). In contrast, the concentrations of Cu periodically observed in clams at stations 1 and 4 in South Bay were 30 times background (Luoma, unpublished data) and the highest Cu levels were as high as any observed in the English clams. The high degree of biological Cu enrichment in some parts of South Bay suggested the benthic community of this portion of the estuary was especially vulnerable to Cu input,

LUOMA AND CAIN: TRACE METAL CONTAMINATION

probably due to undefined physicochemical characteristics of the system.

Silver and copper dynamics of M. balthica. Between March 1975 and February 1978, concentrations of Ag in clams at station 1 varied by over 30 times (from 7 to 220 $\mu\text{g}\cdot\text{g}^{-1}$) and concentrations of Cu by six times (74 to 440 $\mu\text{g}\cdot\text{g}^{-1}$, Fig. 3). Copper concentrations in the clams varied by five times during the same period at station 5 (Fig. 4). Concentrations of Ag were too low at station 5 for assessments of the range of variation to be meaningful. The variation of Cu and Ag concentrations in the animals did not follow the variations of concentrations in the sediments.

The highest concentration of Cu observed in *M. balthica* occurred at station 1 in August 1975 (Fig. 3). This peak coincided with a period of severe anoxia on the mudflat (due to an intense bloom of the benthic macro-algae *Polysiphonia* sp.) which destroyed all but a few isolated patches of the benthic infauna (see also Nichols 1979). Mobilization of biologically available Cu

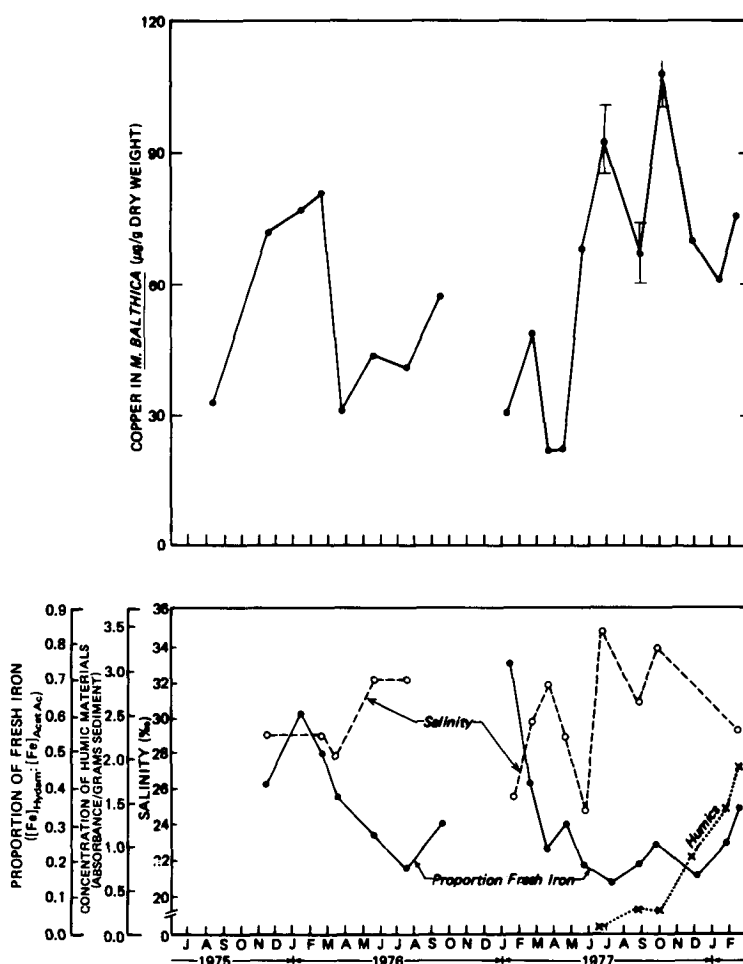


Fig. 4. Salinity, the proportion of freshly precipitated iron oxide in sediments, humic acid concentrations in sediments, and concentrations of copper (Cu) in *Macoma balthica* observed at station 5 between August 1975 and February 1978.

SAN FRANCISCO BAY

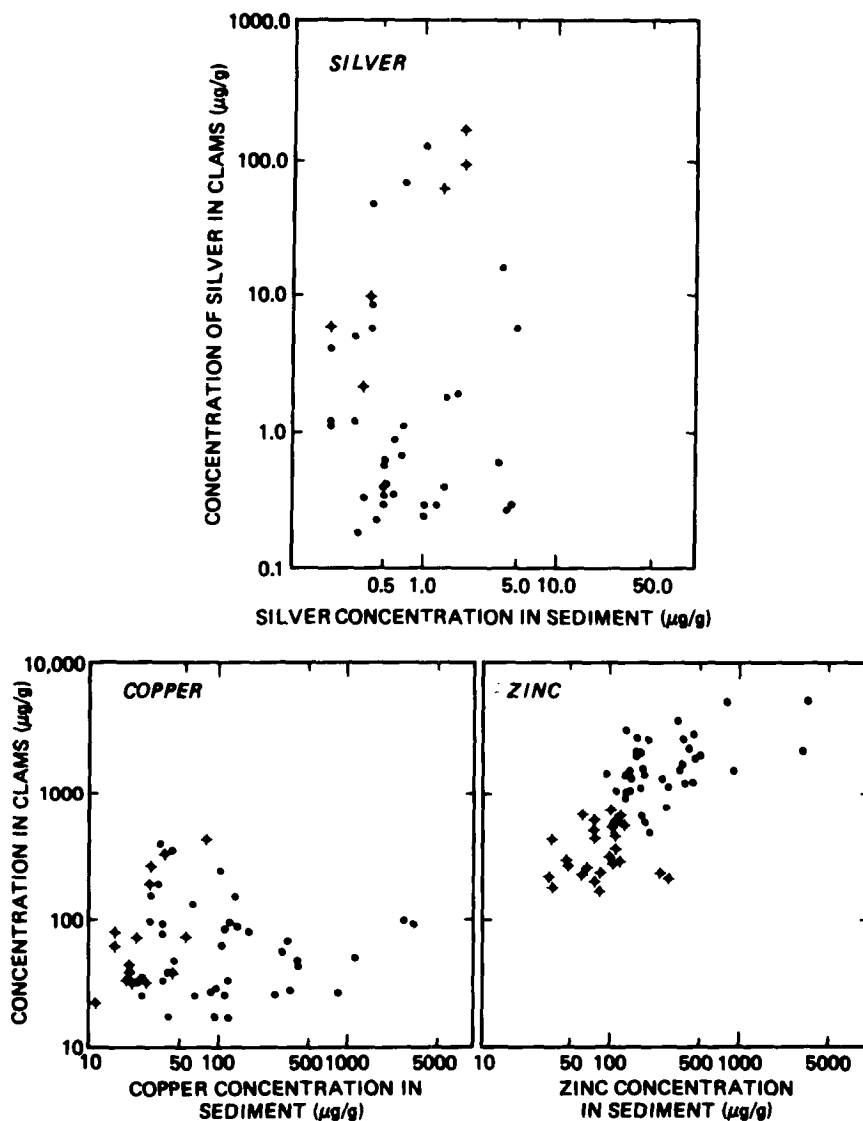


Fig. 5. Concentrations of zinc (Zn), copper (Cu) and silver (Ag) in *Macoma balthica* (\blacklozenge) from San Francisco Bay and *Scrobicularia plana* (\bullet) from southwest England, compared to concentrations of the metals in sediments from the two locations.

has been observed in other estuaries under similar types of anaerobic conditions (Luoma and Bryan in prep.); although the mechanism involved has not been explained.

With the exception of the Cu peak in late 1975, the dynamics of Ag and Cu in *M. balthica* at station 1 followed a similar pattern (Fig. 3). The lowest concentrations of both metals were observed in early summer. Concentrations began to increase with the onset of infrequent rainfall in the late summer and fall. Concentrations peaked in the early winter, followed by a relatively rapid decline, which coincided with the period of maximum rainfall. Temporal variations in Cu concentrations in *M. balthica* at station 5 followed a pattern similar to that observed at station 1 (Fig. 4).

LUOMA AND CAIN: TRACE METAL CONTAMINATION

TABLE 1. CONCENTRATIONS OF AG AND CU IN SEDIMENTS AND CLAMS FROM SOUTH SAN FRANCISCO BAY, COMPARED TO CONCENTRATIONS OBSERVED IN A RELATIVELY PRISTINE HARBOR ON THE PACIFIC COAST.^a

Station	Silver Concentrations ($\mu\text{g}\cdot\text{g}^{-1}$)		Copper Concentrations ($\mu\text{g}\cdot\text{g}^{-1}$)	
	Sediment (mean)	<i>M. balthica</i> (median)	Sediment (mean)	<i>M. balthica</i> (median)
1	1.8	104	52 ± 9	252
2		14	no data	45
3	0.4	7	36 ± 12	83
4		13	100 ± 44	231
5	0.1	6	29 ± 9	65
6		7	22 ± 10	48
7		4	33 ± 13	46
8	0.3	2	42 ± 6	38
9		3.5	92	25
Princeton Harbor		1.2	15	8

^a Silver analyses of sediments were conducted by Girvin, et al., using Zeeman spectroscopy.

The autumn buildup of Cu and Ag in the clams was apparently caused by the influx of local runoff into South Bay. In both 1976 and 1977 the onset of metal accumulation at both stations followed early storms in the watershed of South Bay. Moreover, the concentration of Ag and Cu in the animals, between the time of minimum and maximum concentration in each year, was a function of cumulative rainfall during that period of the year (Fig. 6). If Ag and Cu enter South Bay primarily in runoff, then cumulative rainfall should be an indirect measure of the sum of the metal discharge into South Bay at a given point during the year. The concentration of Cu and Ag in the clams at a given quantity of rainfall (i.e. quantity of metal discharged) was significantly greater in 1977 than in 1976, and (for Ag) slightly higher in 1976 than in 1975. Fresh-water discharge from all sources declined between 1975 and the end of 1977 (Fig. 2) suggesting an inverse relationship between the rate of fresh-water discharge and the accumulation of Cu and Ag in the clams per unit metal discharge in runoff. To quantify this relationship, a metal discharge index, M_d , was calculated for each sampling date between the time of minimum and maximum Ag and Cu concentrations in the clams where

$$M_d = (\Sigma R) (1/FW_d)$$

with ΣR = cumulative rainfall (cm) over the stated period and FW_d = the discharge rate of fresh water ($\text{m}^3\cdot\text{s}^{-1}$) from a specified source. The concentrations of Ag in the clams from station 1, as observed during the period of accumulation in all three years of the study, fell into a single, highly significant regression with the metal discharge index (Fig. 7) when FW_d was determined from Delta discharge 10 days before the sampling date (the 10-day lag was chosen somewhat arbitrarily, but made little difference in the discharge value chosen). The correlation with Ag concentrations in the clams was insignificant when FW_d was determined from San Francisquito Creek discharge within the week prior to sampling, or as the mean discharge rate of the creek for either the 10 or 20 days before the sampling date. Copper concentrations at both station 1 and station 5 also showed highly significant correlations with the metal discharge index when Delta discharge was used for FW_d

SAN FRANCISCO BAY

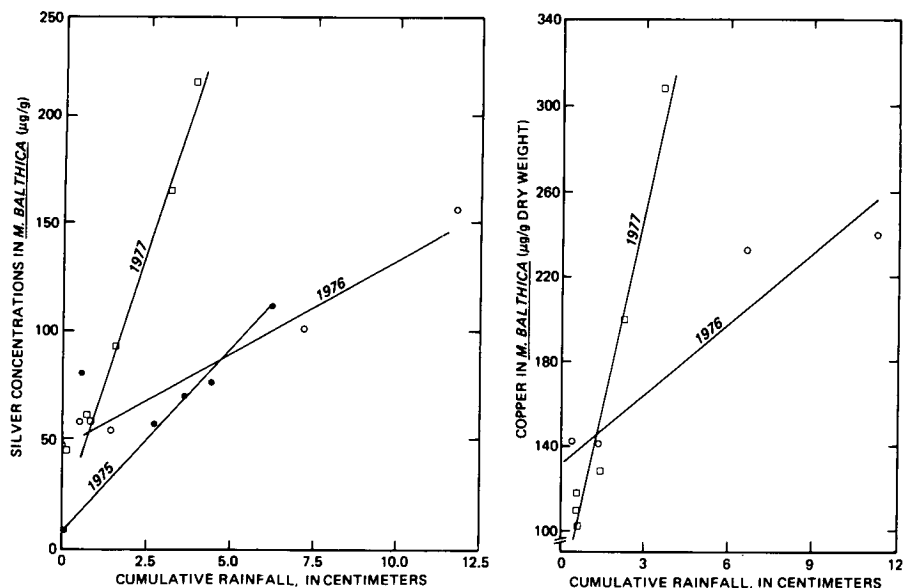


Fig. 6. Correlation of silver (Ag) and copper (Cu) concentrations in *Macoma balthica* from station 1 with cumulative rainfall in 1975, 1976 and 1977. Data are taken from the time between minimum metal concentrations and maximum metal concentrations in the animals in each year. Data for Cu are not presented from 1975 due to the effects of anoxia on Cu concentrations at station 1 in that year.

(Fig. 7). There was no significant difference between the slopes of the relationships at the two stations; however, Cu concentrations at station 1 were consistently higher than those at station 5.

Zinc dynamics. The dynamics of Zn in *M. balthica* at stations 1 and 5 differed from the dynamics of Ag and Cu in several ways (Fig. 8). (1) The period of low discharge was characterized by declining or stable Zn concentrations in the clams. Zinc accumulation in the animals did not begin until after the period of maximum fresh-water discharge, and was not related to cumulative rainfall. (2) The magnitude of the winter peaks in Zn concentration declined as fresh-water discharge declined over the course of the drought. (3) Whereas Cu and Ag concentrations in the clams showed no consistent relationship with salinity, temporal fluctuations in Zn concentrations were consistently the inverse of temporal fluctuations in salinity. (4) Zn concentrations in *M. balthica* were more similar at stations 1 and 5 throughout the study period than were Cu and Ag concentrations.

DISCUSSION

Biologically significant points of Ag and Cu enrichment occur in South Bay. The Ag enrichment is largely the result of Ag discharge from a point source on the western shoal of the southernmost reaches of the Bay. Copper enrichment appears to result from undefined physico-chemical conditions in the Bay, which make the system especially susceptible to the relatively small discharges of Cu. Zinc does not appear to be a contaminant of great significance but its behavior is of interest in that it differs significantly from Ag and Cu. The concentrations of Cu and Ag observed at station 1 in November 1977, were as high as any ever reported for tellenid clams. Within two months of this peak, adult *M. balthica* essentially disappeared from the mudflat at this station (but not from station 3 where metal concentrations are lower). Proving that trace

LUOMA AND CAIN: TRACE METAL CONTAMINATION

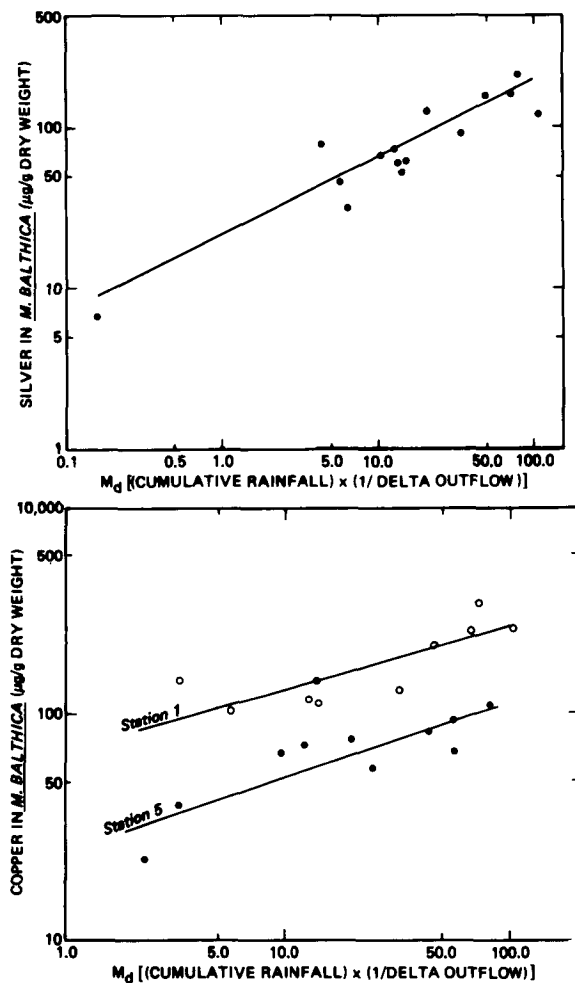


Fig. 7. Correlation of silver (Ag) concentrations at station 1 and copper (Cu) concentrations at stations 1 and 5 with the metal discharge index, M_d . Regression statistics: for Ag, $r = 0.91$ and $\log y = 24 + 0.45 \log x$; for Cu at station 1, $r = 0.79$ and $\log y = 69 + 0.26 \log x$; for Cu at station 5, $r = 0.87$ and $\log y = 25 + 0.31 \log x$. All correlations are significant ($p < 0.01$).

contaminants are affecting organisms in a natural system is nearly an impossible task (Nichols 1979; Luoma 1977b). However, the coincident occurrence of high tissue concentrations of two potent toxicants, and the disappearance of a population suggests the Cu and Ag enrichment in South Bay is worth further investigation.

Fresh-water discharge rates were very important in determining the degree of biological Ag and Cu contamination at least at stations 1 and 5. The accumulation of Cu and Ag in the clams as rainfall increased in frequency through the summer and fall, and the annual correlation between metal concentrations in the clams and cumulative rainfall, suggested local runoff provided the primary input of the two metals. This was substantiated by the observation by Girvin et al. (unpublished data) of elevated concentrations of Ag in solution at a location offshore from our station 1 (where our data indicate biological contamination is diluted relative to station 1) in

SAN FRANCISCO BAY

September 1976, following a rainstorm. Three days later the high concentrations of Ag had disappeared. In a diel study at the same station they also observed increasing concentrations of Ag in solution with the onset of rainfall.

The rate of fresh-water discharge also had an inhibitory effect on biologically available Cu and Ag during the summer and fall period. The year of lowest fresh-water discharge was the year when metal accumulation in the clams per unit rainfall was greatest. Moreover, 60-80% of the temporal variance in the summer-fall concentrations of Ag and Cu in the clams was explained by our metal discharge index, which included the inverse of Delta discharge as one term. The correlation with the metal discharge index suggested concentrations of Cu and Ag available to *M. balthica* in South Bay between 1975 and 1978 were controlled during the summer-fall period by a dynamic balance between metal input rates from local runoff and a slow rate of metal loss, modulated by fresh-water discharge rates. (Of course, the input and loss functions need not represent metal loadings alone, but could also occur through chemical changes in the sediments or water column that enhance or decrease the biological availability of the metals.) The magnitude of the fresh-water discharge during this period of relatively long water residence times in South Bay, appeared to be the crucial factor determining the size of the annual peak in Cu and Ag concentrations.

The rapid decline of Cu and Ag concentrations in the clam tissues during winter and spring occurred as significant quantities of fresh-water and terrigenous sediment entered South Bay. The

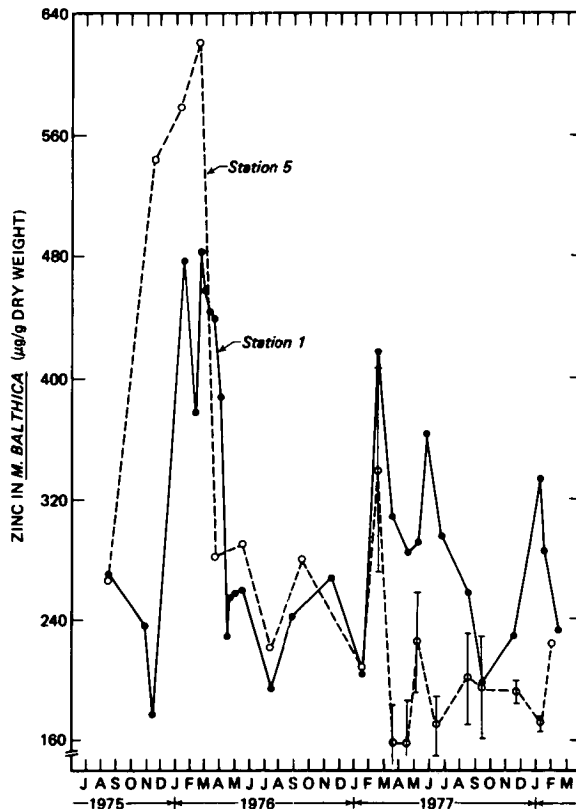


Fig. 8. Zinc (Zn) concentrations in *Macoma balthica* at stations 1 and 5 between August 1975, and February 1978.

LUOMA AND CAIN: TRACE METAL CONTAMINATION

onset of the decline in Cu concentrations at station 5 coincided with the minimum salinity observed at that station in 1975-76 and with the onset of declining salinity and increasing humic acid concentrations in the sediments in 1977-78. At station 1 the onset of the 1975-76 decline coincided with a salinity decline and a gradual increase in the proportion of freshly precipitated iron oxide in the sediment. In 1977-78 the decline did not occur until salinities fell below 26 ‰, but coincided with a sharp increase in the humic acid content of the sediments. The 1976-77 decline at station 1 did not coincide with a salinity decline, but the proportion of freshly precipitated iron in the sediment did rise as Ag and Cu levels in the clam began to drop.

There are at least two possible explanations for the decline in Ag and Cu concentrations in the animals. First, at some point in the early winter, the flushing action of fresh-water discharge is sufficiently strong to remove biologically available Cu and Ag from South Bay as rapidly as it enters in the runoff. By limiting the residence time of the contaminated water and/or sediment, the exposure of the clams to Ag and Cu is limited. The second possibility is that as the rainy season progresses the chemical and/or physical nature of the terrigenous sediment in the runoff changes (V. Kennedy pers. comm.). Early runoff should be dominated by sediment from the urban watershed of South Bay. Not only will the initial storms wash urban streets containing several months' accumulation of contaminants, but also the initial rainfall of the year in the less urbanized areas will largely be converted to groundwater, rather than running off, until the soils are saturated. An example of the latter was observed after the first storm of the year in September 1977, when no stream flow was detected in either San Francisquito Creek or Redwood Creek (USGS Data Report, in prep.) at gauging stations upstream from most of the urban area. However, a significant pulse of flow was observed at an urban gauging station in Stevens Creek (Santa Clara Valley Water District unpublished data). Later in the rainy season the urban runoff will carry less sediment, but more important, the stream discharge will also carry a heavy load of less contaminated sediment from the more rural parts of the watershed. Humic acids should be more concentrated in the rural runoff than in the urban runoff; the close correspondence of declines in Ag and Cu concentrations in 1977-78 with increased humic acid concentrations could reflect a change in the dominant sediment type in the runoff. These hypotheses are, of course, not mutually exclusive since any flushing modulated by fresh-water discharge would also be important in removing urban runoff from the estuary.

The metal discharge index represents a first step toward quantifying the degree of Cu and Ag enrichment we might expect in South Bay organisms as fresh-water discharge into the estuary is reduced. Unfortunately, the index will not be useful in predicting environmental impact until we understand more about the relative importance in flushing of South Bay by local stream discharge versus Delta discharge. Initial model studies of hydrodynamics in South Bay suggest significant quantities of fresh water from the Delta should not have penetrated beyond San Bruno shoals during the summer or fall in either 1976 or 1977 (Imberger et al. 1977). If so, local stream discharge is the most likely source modulating the different rates at which biologically available Cu and Ag were removed from South Bay in these two years. The winter decline in concentrations of Cu also clearly followed major pulses of local runoff more closely than Delta discharge at station 5 in March 1976, and November 1977, and at station 1 in January, 1977 (although the chemical nature of the sediment in the runoff may also explain these effects). Several lines of evidence raise questions about the dominance of local stream discharge as a cleansing force in South Bay, however: (1) The lowest Ag concentrations ever observed at station 1 followed a period of zero rainfall between 1 May and 20 June 1975. The Ag minimum suggests a negligible input of Ag combined with a rapid flushing of available Ag at this time. Local stream flow declined to relatively low levels by June 1975; but Delta discharge peaked at a sufficient rate to penetrate San Bruno shoals shortly before the Ag minimum. At least in the spring of 1975, Delta discharge was the most likely

SAN FRANCISCO BAY

force driving the removal of biologically available Ag at station 1. (2) The salinity anomaly in August 1977, was clearly not the result of local runoff. This salinity minimum coincided with a small influx of terrigenous sediment (reflected by an increase in the proportion of freshly precipitated iron) at both stations 1 and 5, but, more importantly, with a sharp reduction in Cu concentrations in clams at station 5. A similar reduction in Cu concentrations at station 8 was observed at this time, but not at stations 1, 3 or 6 (Luoma and Cain unpublished data). (3) When the metal discharge index was calculated from the inverse of local stream flow, no correlation with the three years of data on Cu and Ag levels in the clams was observed. It is possible that we did not adequately quantify crucial aspects of the highly irregular stream flows in the relationship; but it is also possible that Delta discharge is a more important flushing force on the shoals of the South Bay than predicted from the initial studies of Imberger et al. (1977) in the main channel of the estuary.

The differences between Zn dynamics and the dynamics of Cu and Ag in South Bay demonstrate that all trace metals do not behave similarly in the system. The differences between the metals may reflect their source, or the source of the chemical factors that control their availability. In 1977-78, Zn concentrations in the clams were lower at both stations than in 1975-76, and, like Cu, concentrations at station 1 exceeded those at station 5 approximately twofold. The distribution of Zn and Cu in 1977-78 suggest factors controlling the availability of the metals originated from similar local sources, probably throughout South Bay (since the northward dilution of Ag greatly exceeded that of Cu and Zn). The south-to-north gradient in Cu and Zn concentrations in 1977-78 could reflect differences in discharge rates, dilution by an increasing volume of water toward the north, or more efficient flushing in the northern reaches. The similarity of the slopes of the regressions between Cu in the clams versus M_d at stations 1 and 5 suggests one of the latter two suggestions is most likely.

In contrast to Cu, the south-to-north gradient for Zn was not observed in 1975-76 when Delta discharge was certainly sufficient to flow southward of San Bruno shoals. Zinc concentrations at station 5 exceeded those at station 1 in 1975-76, and peak concentrations at both stations were much greater than in the following years of low fresh-water discharge. Although further study is required, it appears that Delta-derived water may control the biological availability of Zn in years of normal rainfall. This hypothesis is consistent with our earlier suggestion that Zn is not discharged in sufficient quantities into South Bay to be a biologically significant contaminant.

Factors such as temperature, salinity (Wolfe 1971; Phillips 1977a), and biological phenomena (tissue growth; seasonal variations in physiology—Frazier 1975; Betzer and Pilson 1975; Phillips 1977b), have also been cited to explain temporal variations in the metal concentrations of benthic organisms within estuaries. In South Bay, temperature was not found to affect Zn, Ag or Cu concentrations in *M. balthica* directly. The temporal pattern of variation in metal concentrations was roughly the inverse of the seasonal temperature cycle. Seasonal contrasts in the relationship with Cu and Ag concentrations also suggested salinity was not a variable to which these metals were directly responding. Concentrations of Cu and Ag in the clam varied inversely with salinity at station 1 in the spring (March, April 1976; April 1977) and positively with salinity at both stations 1 and 5 in the winter. Zinc concentrations in the clam varied inversely with salinity in a consistent manner; thus, the possibility that salinity variations may have had some direct effect on Zn uptake rates by *M. balthica* cannot be discounted.

The winter decline in Cu and Ag concentrations in the clams coincided with the period of maximum growth of the organism (Nichols in prep.; Cloern and Nichols 1978). Two arguments suggest the effects of tissue growth on metal concentrations were minimal, however: (1) temporal changes in the content (μg) of Ag and Cu in the animals closely followed changes in concentration ($\mu\text{g}\cdot\text{g}^{-1}$), thus eliminating the possibility that the seasonal differences in metal concentrations were

LUOMA AND CAIN: TRACE METAL CONTAMINATION

the result of simply a changing tissue mass, rather than metal fluxes; and (2) sharp changes in the Cu concentrations of *M. balthica* were not observed during the spring at stations 6 and 8 in 1977 (Luoma and Cain unpublished data). If undefined physiological processes were responsible for the temporal changes observed, those processes were specific to stations 1 and 5 - a highly unlikely prospect.

Our evidence strongly suggests that the interaction of hydrodynamic processes, local weather, and, quite possibly, the chemical characteristics of sediments entering South San Francisco Bay in local runoff, play the major roles in controlling the contamination of organisms south of the San Mateo Bridge with Cu and Ag. The rate of fresh-water discharge into the Bay is a primary factor mitigating the effects of those interactions, and appears to control the amplitude of the annual peak in contaminant concentrations.

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SAN FRANCISCO BAY

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