

Trace Metal Associations in the Water Column of South San Francisco Bay, California

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Spatial distributions of copper (Cu), zinc (Zn) and cadmium (Cd) were followed along a longitudinal gradient of dissolved organic carbon (DOC) in South San Francisco Bay (herein referred to as the South Bay). Dissolved Cu, Zn and Cd concentrations ranged from 24 to 66 nM, from 20 to 107 nM and from 1.2 to 4.7 nM, respectively, in samples collected on five dates beginning with the spring phytoplankton bloom and continuing through summer, 1985. Dissolved Cu and Zn concentrations varied indirectly with salinity and directly with DOC concentration which ranged from 2.1 to 4.1 mg l⁻¹. Available thermodynamic data strongly support the hypothesis that Cu speciation may be dominated by association with dissolved organic matter. Analogous control of Zn speciation by organic complexation was, however, not indicated in our computations. Computed free ion activity estimates for Cu, Zn and Cd were of the order of 10⁻¹⁰, 10⁻⁸ and 10⁻¹⁰ M, respectively. The availability of these metals may be among the factors regulating the growth of certain phytoplankton species within this region of the estuary. In contrast to dissolved Cu, dissolved Cd was directly related to the concentration of suspended particulate matter, suggesting a source of dissolved Cd coincident with elevated particle concentrations in the South Bay (e.g. runoff and solute desorption). Consistent with work in other estuaries, partitioning of all three trace metals onto suspended particulates was negatively correlated with salinity and positively correlated with increases in particulate organic carbon associated with the phytoplankton bloom. These results for the South Bay indicate that sorption processes influence dissolved concentrations of these trace metals, the degree of this influence varies among metals, and processes controlling metal distribution in this estuary appear to be more element-specific than spatially- or temporally-specific.

Introduction

Understanding the transport and distribution of solutes in estuaries is for many reasons a highly complicated task. This environmental complexity is very evident in studies of trace metal reactions in estuaries. Hydrodynamic processes affect sediment transport and, thus, metal sorption processes (Delfino & Otto, 1986; Helz & Sinex, 1986). Advective transport

influences movement of certain metals from bottom sediment pore waters (Delfino & Otto, 1986). Coagulation of riverine particles may remove trace metals from solution, or particle-bound metals may be desorbed as salinity increases (Salomons, 1980; Li *et al.*, 1984; Ackroyd *et al.*, 1986). These sorbed metals may be associated with various mineral phases, e.g. clays (Gibbs, 1986), oxide coatings (Balls, 1986), or with particulate organic matter (Davis, 1984, Laxen, 1985; Wangersky, 1986). In the solution phase, speciation of metals may be affected by organic complexation (van den Berg *et al.*, 1987). The transport of degraded plant material and the influx of marine humic acids associated with algal blooms have been implicated as important sources of such organic complexing agents in estuaries (Delfino & Otto, 1986; Jones *et al.*, 1986). Although physical and chemical factors affect primary productivity, algae and other microbes may in turn alter trace element cycling. The biota may serve as a source of organic chelators (Lumsden & Florence, 1983), a sink for solute sorption (Boyle *et al.*, 1982; Froelich *et al.*, 1985; Kuwabara *et al.*, 1986) and a catalyst for particle flocculation and sedimentation (Sholkovitz, 1976; Avnimelech *et al.*, 1982).

As one of the largest estuarine systems in the world to experience the effects of urban and industrial development, San Francisco Bay exemplifies the complexity of estuaries. It has been described as a three-component system: the northern reach (including the Suisun and San Pablo Bays), the Central Bay and the South Bay (Conomos, 1979). Temporal trends in primary productivity, biomass and species composition in the northern reach are significantly influenced by physical processes related to freshwater input from the Sacramento and San Joaquin Rivers. In comparison, phytoplankton biomass in the South Bay is more sensitive to grazing pressure as well as to the physical effects of tidal fluctuation and river discharge (Cloern *et al.*, 1985). Although the South Bay is typically well mixed, an algal bloom occurs each spring concurrent with the establishment of a vertical salinity gradient.

Several studies have examined the spatial and temporal distributions of dissolved trace metals within San Francisco Bay. In the northern reach, Eaton (1979a) observed that dissolved trace metal distributions reflected physical mixing, chemical removal and multiple inputs within the estuary. Gordon (1980) reported conservative mixing of dissolved trace metals in the northern reach and an undefined metal source in the upper estuary at low salinities. Girvin *et al.* (1978) observed a concentration gradient for dissolved Cd, Cu and Zn in the South Bay and a temporal increase in concentrations during the spring and summer during two drought years. In general, Cd was found to be predominantly partitioned in the dissolved phase, Cu was about equally associated with the solid and solution phases, and Zn was primarily particle-bound.

In this paper we assess potentially important mechanisms that control trace metal distribution in the water column of South San Francisco Bay. Chemical, biological and physical data are examined from five sampling surveys conducted between the spring algal bloom period of March 1985, and September 1985. Large climatic and hydrographic changes occur between sampling dates as a result of the well-defined wet and dry seasons, and dramatic changes in many chemical and physical parameters result, in part, from changes in phytoplankton density (Table 1). The data indicate that, (1) Cu speciation is regulated by complexation with dissolved organic matter (DOM), (2) elevated dissolved Cd appears to be coincident with elevated suspended particulate mass concentrations, but less dissolved Cd is observed when particles with elevated POC are present, and (3) temporal and spatial variability in the chemical character of the DOM and mineralogical composition of the suspended sediment are not pronounced.

TABLE 1. Physical and chemical parameters collected from five sampling cruises in the South San Francisco Bay in 1985 including: suspended particulate mass in mg l^{-1} (SPM), chlorophyll-a in $\mu\text{g l}^{-1}$ (CHL-a), particulate organic carbon in $\mu\text{g l}^{-1}$ (POC), dissolved organic carbon in mg l^{-1} (DOC), salinity in g solid per g solution (SAL), and dissolved and particulate trace metal concentrations. Confidence intervals (95%, N=3) for trace metal concentrations about the mean are also presented. Station numbers refer to midchannel sampling sites as depicted in Figure 1, with increasing numbers corresponding to a southward direction away from the estuary mouth. The column for freshwater discharge data (DIS) represents in $\text{m}^3 \text{s}^{-1}$ the sum of freshwater inputs to the South Bay by local riverine and municipal sewage treatment sources. The percent DIS attributable to water treatment plant effluent is given in parentheses.

Date	DIS	Station No.						Dissolved (nM)			Particulate (pg g^{-1})		
			SPM	CHL-a	POC	DOC	SAL	Cu	Zn	Cd	Cu	Zn	Cd
29/3/85	(31)	27	11.3	21.5	1250	2.9	0.0250	47 ± 3	32 ± 3	1.2 ± 0.4	45.3 ± 0.5	43.2 ± 3.2	0.36 ± 0.01
		30	13.5	35.2	1720	3.6	0.0234	55 ± 5	57 ± 3	2.4 ± 0.4	56.1 ± 1.8	79.5 ± 4.5	0.83 ± 0.01
		32	16.1	32.4	1870	3.5	0.0220	53 ± 6	61 ± 3	2.8 ± 0.4	54.1 ± 2.9	87.6 ± 1.0	0.87 ± 0.01
		36	17.2	37.4	1180	4.0	0.0197	66 ± 5	107 ± 5	4.4 ± 0.2	65.2 ± 0.9	154.1 ± 8.0	1.58 ± 0.03
16/4/85	(79)	27	2.1	7.3	400	2.7	0.0271	55 ± 2	43 ± 8	2.3 ± 0.2	51.1 ± 2.0	54.8 ± 3.8	0.59 ± 0.01
		30	2.4	5.0	390	2.8	0.0261	58 ± 3	49 ± 5	2.8 ± 0.5	50.9 ± 2.9	63.7 ± 2.6	0.69 ± 0.02
		32	7.9	9.5	540	2.8	0.0250	53 ± 9	50 ± 5	2.8 ± 0.4	48.8 ± 3.5	65.7 ± 0.8	0.81 ± 0.02
		36	11.6	6.3	530	3.0	0.0223	58 ± 6	62 ± 8	4.3 ± 0.4	53.3 ± 1.2	85.0 ± 2.4	1.41 ± 0.05
29/4/85	(83)	27	3.5	2.9	230	2.6	0.0268	53 ± 8	47 ± 5	3.1 ± 0.5	46.7 ± 7.9	60.4 ± 2.0	0.83 ± 0.06
		30	2.1	2.8	250	2.6	0.0265	57 ± 2	43 ± 3	3.1 ± 0.4	48.1 ± 0.7	54.8 ± 5.1	0.81 ± 0.05
		32	9.0	3.6	370	2.4	0.0261	44 ± 6	46 ± 9	3.6 ± 0.2	38.2 ± 3.9	58.0 ± 2.2	1.12 ± 0.06
		36	8.5	1.7	300	2.6	0.0245	57 ± 2	49 ± 5	4.0 ± 0.7	46.6 ± 2.3	64.0 ± 1.5	1.26 ± 0.15
9/7/85	(88)	27	0.1	1.2	200	2.0	0.0301	46 ± 2	20 ± 6	2.1 ± 0.3	39.6 ± 1.0	21.5 ± 2.7	0.51 ± 0.01
		30	0.6	1.0	180	2.3	0.0295	49 ± 3	31 ± 8	2.3 ± 0.4	41.0 ± 1.7	36.3 ± 4.4	0.54 ± 0.02
		32	2.8	1.5	250	2.3	0.0290	46 ± 2	34 ± 3	2.4 ± 0.1	41.2 ± 2.2	39.6 ± 4.1	0.65 ± 0.03
		36	9.3	1.5	330	3.1	0.0271	49 ± 2	37 ± 1	3.6 ± 0.1	44.2 ± 2.0	45.0 ± 4.0	1.06 ± 0.03
10/9/85	(88)	27	1.9	1.9	200	2.1	0.0316	39 ± 2	32 ± 3	1.4 ± 0.1	32.9 ± 1.1	36.6 ± 2.6	0.36 ± 0.02
		30	2.0	1.2	200	2.1	0.0316	39 ± 2	32 ± 2	2.0 ± 0.4	34.1 ± 1.0	37.1 ± 4.0	0.48 ± 0.03
		32	4.5	2.4	250	2.1	0.0311	36 ± 3	44 ± 2	2.7 ± 0.2	32.0 ± 0.8	50.7 ± 6.8	0.70 ± 0.09
		36	20.7	7.2	400	2.4	0.0286	24 ± 5	47 ± 6	4.7 ± 0.3	22.1 ± 0.5	53.2 ± 3.3	1.40 ± 0.55

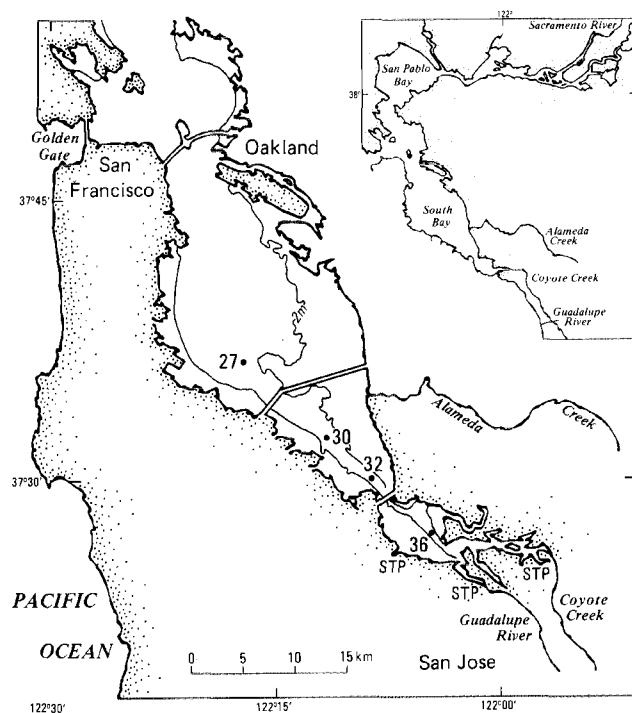


Figure 1. Midchannel sites in South San Francisco Bay where surface water was sampled to examine processes affecting trace metal distributions. Major freshwater sources from riverine and sewage treatment plant (STP) inputs are also depicted. Longitude and latitude is shown for the South Bay and in the figure insert, which provides an overall view of the Bay.

Materials and methods

On each of five sampling dates, surface water (1 m depth) was collected from a small fiberglass boat at four mid-channel stations along the longitudinal axis of South San Francisco Bay for trace metal and organic carbon analyses. Subsequent reference to sampling sites in the text, tables and figures are in terms of U.S. Geological Survey Sampling Station numbers 27, 30, 32 and 36 (Figure 1) with higher station numbers representing greater southward distance from the estuary mouth at the Golden Gate Bridge (31.2, 42.4, 48.9 and 57.0 km, respectively, along the centre of the main channel). Mean lower low water depths for Stations 27, 30, 32 and 36 were 11.0, 12.2, 13.1, and 7.0 m, respectively. Additional surface water samples were collected simultaneously from a research vessel positioned approximately 100 m downstream from the small boat. These samples were analysed for salinity (Lewis, 1980) and concentrations of particulate organic carbon (POC), suspended particulate matter (SPM), and chlorophyll-a, using methods specified by Wienke and Cloern (1987).

Immediate initial processing of surface water samples for dissolved and suspended particulate analyses was done onboard. Suspended particles were collected on acid-washed 142-mm diameter, 0.4 µm pore size polycarbonate filters (Nuclepore). Particulate-bound trace metals were extracted with 0.1 N nitric acid (HNO₃) for 2 hr. Quartz-distilled HNO₃ (6 M) contained $<2 \times 10^{-9}$ M total Cu or Zn and $<1 \times 10^{-10}$ M

total Cd. After particles were separated from the extractant by filtration, the filtrate was refrigerated for subsequent trace element analysis. Samples for dissolved organic carbon (DOC) analysis were filtered through furnace-treated glass fiber filters (Whatman GF/D) and preserved by refrigeration and addition of c. 50 μ l of a saturated mercuric chloride solution per 20 ml sample. DOC was measured on a Dohrmann carbon analyzer by persulfate and ultraviolet oxidation. Dissolved trace metal samples were filtered through acid-washed 47 mm diameter, 0.4 μ m pore size polycarbonate membranes. A fluoroethylene polymer filter holder mounted on a resin kettle (Kuwabara, 1980) was used to minimize metal contamination during sample processing. After filtration, samples were acidified to pH 2 with HNO₃ and refrigerated. Dissolved trace metals were extracted and concentrated by a cobalt coprecipitation method (Bloom & Crecelius, 1984). Trace metal analyses were performed by stable platform graphite furnace atomic absorption spectroscopy with Zeeman correction. Confidence intervals (95%, N=3) for trace metal measurements were typically <10% of the mean concentration (Table 1). However, confidence intervals for dissolved Cd concentrations, with low mean concentrations relative to other metals, were as high as 33% of the mean.

Initial observations of dissolved and particulate trace metal distributions indicated a need to examine the spatial and temporal variability of the chemical composition of inorganic suspended particles and DOC. On three subsequent dates at Stations 27 and 32 (Figure 1), gram quantities of suspended sediment were collected by hollow fiber tangential flow filtration (Kuwabara & Robinson, 1987) for major elemental analyses by lithium metaborate fusion after sequential extraction (Tessier *et al.*, 1979; Lichte *et al.*, 1987). Sediment samples (before extraction) were also analyzed by X-ray diffraction for mineralogy. As a crude indication of the spatial and temporal variability in the chemical character of the DOC in the South Bay, DOC was also extracted to determine concentrations of humic substances (Thurman & Malcolm, 1981) on these dates.

Results

The minimum salinity observed in the South Bay during any sampling was 0.0197 (expressed herein in terms of g solids per g solution, or 10³ ppt). Salinity increased with proximity to the mouth of the Bay in all five profiles, as expected in the main channel. Although the spring phytoplankton bloom in March was distinctively represented by elevated chlorophyll-a and POC concentrations (Tables 1 and 2), spatial trends for both parameters were not consistent. Both chlorophyll-a and POC generally increased with decreasing salinity in individual profiles, but the concentrations sometimes peaked at Station 32 rather than 36 (the southern-most sampling site) or decreased from Station 27 to 30.

Dissolved organic carbon concentrations usually increased away from the estuary mouth (i.e. going southward), mirroring salinity (Table 1). DOC concentrations generally decreased from spring through the summer. Spatial trends in dissolved Cu concentration were not pronounced and did not consistently follow SAL on any cruise (Figure 2b). In March cruise, a weak increase in dissolved Cu occurred with distance away from the estuary mouth, and the September cruise showed the opposite trend. There was a slight southward increase in dissolved Zn concentration, which was most discernible during March (Figure 2b). Dissolved Cd increased toward the south in all profiles, but in contrast to Cu and Zn, that increase was pronounced in September (Figure 2c). Assessment of

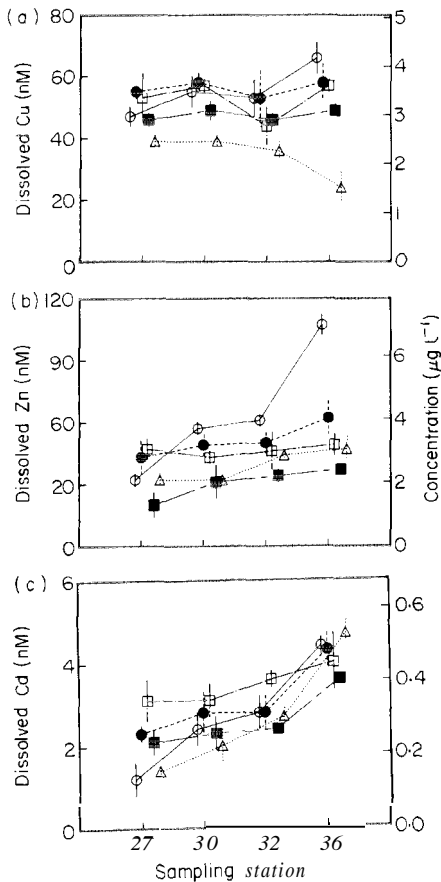


Figure 2. Spatial and temporal distributions of dissolved Cu, Zn and Cd ((a), (b) and (c) respectively) on each of five sampling dates beginning with the spring period of high phytoplankton biomass and high freshwater inflow, continuing through the summer period of low phytoplankton biomass and reduced freshwater inflow. [Data from the five sampling cruises on (○) March 29, (●) April 16, (□) April 29, (■) July 29 and (△) September 10, 1985 are represented by open circles, shaded circles, open squares, shaded squares and triangles, respectively.]

temporal changes in metal concentrations at individual sites must be interpreted carefully, because samples were not taken during the same tidal phase on different sampling dates.

Linear regression on data aggregated from the five cruises indicated that approximately 83% of the DOC variance could be explained by changes in salinity (Figure 3a). A similar negative correlation with **SAL** was observed for both dissolved Cu and Zn ($r^2=0.53$ and 0.64 respectively, Figure 3b and 3c). Alternatively, concentrations of these metals correlated positively with DOC ($r^2=0.45$ and 0.66 for Cu and Zn, respectively, Figure 4). Dissolved Cd concentrations were also negatively correlated with **SAL** ($r^2=0.22$), but only weakly when compared to correlations of **SAL** with DOC, dissolved Cu or Zn (Figures 3 and 5). Unlike Cu, dissolved Cd was positively correlated with **SPM** ($r^2=0.33$).

Partitioning coefficients (K_D) were calculated as the ratio of the mass of particulate-bound metal per unit particle mass ($\mu\text{g g}^{-1}$) over the dissolved solute mass per unit solvent volume ($\mu\text{g ml}^{-1}$). Values are expressed in units of ml solvent per g suspended particles.

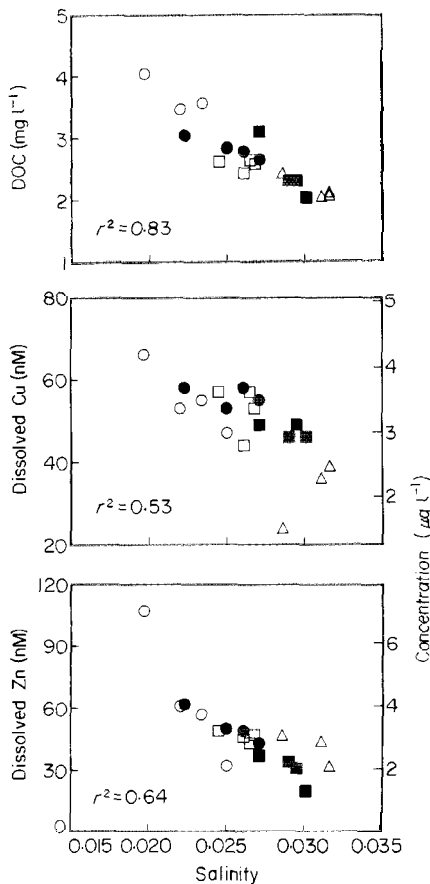


Figure 3. Coincident salinity correlation with DOC, dissolved Cu and Zn ((a), (b) and (c), respectively). Salinity measurements are expressed as g solid per g solution. (Data from the five sampling cruises on (○) March 29, (●) April 16, (□) April 29, (■) July 29 and (△) September 10, 1985 are represented by open circles, shaded circles, open squares, shaded squares and triangles, respectively.)

Partitioning of all three trace metals onto suspended particles decreased with increasing salinity ($r^2 = 0.38, 0.88$ and 0.69 for Cu, Zn and Cd partitioning coefficients respectively, Figure 6). Particle-bound copper also increased with particulate organic carbon ($r^2 = 0.37$, Table 2), suggesting a transient effect on Cu partitioning due to the spring phytoplankton bloom. Particulate-bound metal concentrations in suspended sediment were higher than usually observed in surficial bottom sediment (Bradford & Luoma, 1980; Axtmann, personal communication). This may be due to differences in particle size distribution, since suspended particles typically have smaller mean particle diameters. Eaton (1979b) observed this particle size effect on metal concentrations of San Francisco Bay bottom sediment.

Results from subsequent cruises indicated that percent humic substance by carbon weight relative to total DOC was not statistically different between Stations 27 and 32 or between cruises (Table 3). The distribution of major cations in the suspended sediment was also similar, although spatial similarities appear more striking than temporal ones

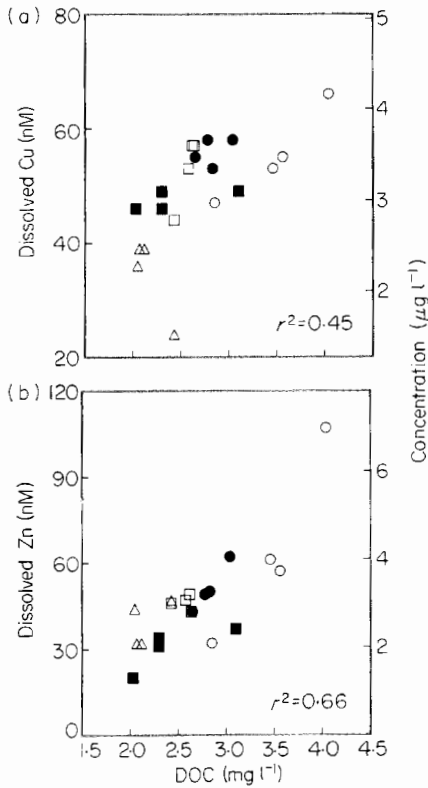


Figure 4. Relationship of dissolved Cu and Zn [(a) and (b), respectively] with DOC. [Data from the five sampling cruises on (○) March 29, (●) April 16, (□) April 29, (■) July 29 and (△) September 10, 1985 are represented by open circles, shaded circles, open squares, shaded squares and triangles, respectively.]

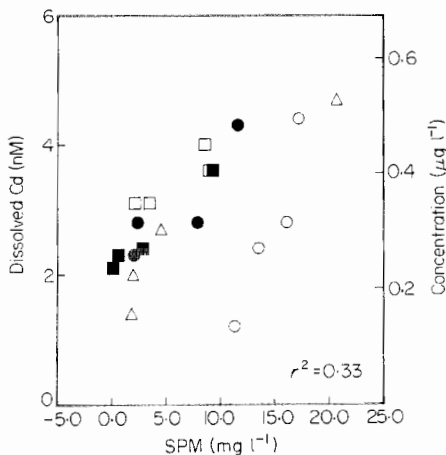


Figure 5. Regression analysis indicating a possible source of dissolved Cd from suspended sediments or undefined sources coincident with SPM (e.g., runoff). [Data from the five sampling cruises on (○) March 29, (●) April 16, (□) April 29, (■) July 29 and (△) September 10, 1985 are represented by open circles, shaded circles, open squares, shaded squares and triangles, respectively.]

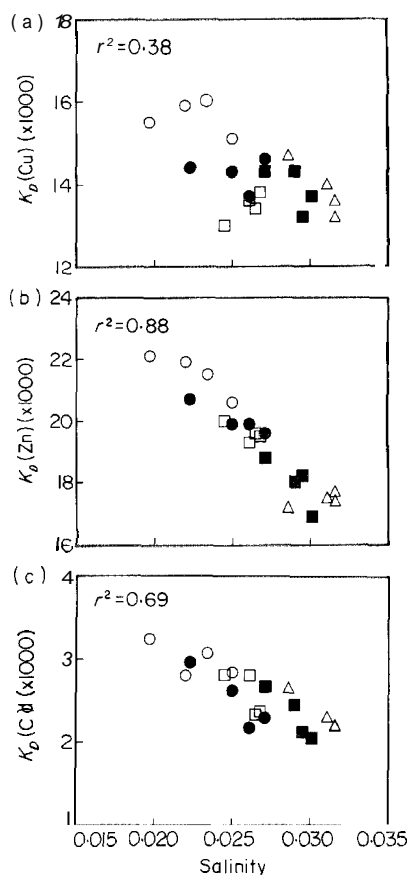


Figure 6. Partitioning of Cu, Zn and Cd [(a), (b) and (c), respectively] on suspended particles in South San Francisco Bay. Partitioning coefficients and salinity are presented in units of ml solution per g particles, and g solid per g solution, respectively. [Data from the five sampling cruises on (○) March 29, (●) April 16, (□) April 29, (■) July 29 and (△) September 10, 1985 are represented by open circles, shaded circles, open squares, shaded squares and triangles, respectively.]

(Table 4). Analyses of suspended sediment by X-ray diffraction indicated that samples from both stations were mineralogically similar, with a predominance of illite and smaller amounts of chlorite and quartz.

Discussion

Cu and Zn

Although Cu and Zn profiles in the South Bay vary considerably between sampling dates (Table 1, Figure 2), analysis of aggregated data from all cruises reveals a number of interesting correlations between measured parameters (Table 2). It is important to note that measured parameters (e.g. SPM, *CHL-a*, POC, DOC and SAL) are not all independent variables (Table 2). Given that particulate organic carbon dominated the suspended particles during the phytoplankton bloom, and that the annual phytoplankton

TABLE 2. Correlation coefficients for parameters measured in South San Francisco Bay (underlined values are significant at the 0.01 level for $N = 20$ per parameter).

	SPM	CHL-a	POC	DOC	SAL	Dissolved			Partitioning Coefficient	
						Cu	Zn	Cd	Cu	Zn
CHL-a	<u>0.68</u>									
POC	<u>0.67</u>	<u>0.95</u>								
DOC	<u>0.67</u>	<u>0.84</u>	<u>0.78</u>							
SAL	<u>-0.65</u>	<u>-0.73</u>	<u>-0.70</u>	<u>-0.91</u>						
Dissolved Cu	<u>-0.01</u>	<u>0.40</u>	<u>0.34</u>	<u>0.67</u>	<u>-0.73</u>					
Dissolved Zn	<u>0.64</u>	<u>0.69</u>	<u>0.52</u>	<u>0.81</u>	<u>-0.80</u>	0.54				
Dissolved Cd	<u>0.57</u>	<u>0.05</u>	<u>-0.04</u>	<u>0.37</u>	<u>-0.47</u>	<u>0.14</u>	<u>0.61</u>			
Cu partitioning	<u>0.72</u>	<u>0.88</u>	<u>0.89</u>	<u>0.76</u>	<u>-0.62</u>	<u>0.20</u>	<u>0.54</u>	0.08		
Zn partitioning	<u>0.52</u>	<u>0.78</u>	<u>0.78</u>	<u>0.90</u>	<u>-0.94</u>	<u>0.78</u>	<u>0.72</u>	0.23	<u>0.63</u>	
Cd partitioning	<u>0.85</u>	<u>0.71</u>	<u>0.68</u>	<u>0.80</u>	<u>-0.83</u>	<u>0.35</u>	<u>0.73</u>	0.50	<u>0.66</u>	<u>0.74</u>

TABLE 3. Results of subsequent sampling cruises to determine the humic substance fraction of the dissolved organic carbon at two stations in the South Bay. Mean values and 95% CI ($N = 6$) are presented for DOC and humic substance data.

Sample Station	Date	DOC (mg l^{-1})	% Humic substances
27	9/6/86	2.1 ± 0.5	44 ± 14
	15/7/86	2.5 ± 0.2	43 ± 4
32	9/6/86	3.0 ± 0.7	39 ± 12
	15/7/86	3.1 ± 0.4	40 ± 7

TABLE 4. Major elemental distribution of suspended sediment expressed in weight percent after sequential extraction, with 95% confidence intervals ($N = 3$). Sediment was initially analyzed in terms of oxide concentrations. Data were then normalized and transposed to the elemental state.

Element	Station 27 13/12/86	Station 27 15/7/86	Station 32 13/12/86	Station 32 15/7/86
Si	28.70 (0.99)	31.88 (0.99)	30.11 (1.50)	31.60 (0.42)
Ti	0.58 (0.02)	0.41 (0.01)	0.50 (0.02)	0.47 (0.02)
Al	10.91 (0.99)	8.89 (0.32)	9.69 (0.79)	9.00 (0.32)
Fe	6.29 (0.30)	4.55 (0.21)	5.94 (0.15)	5.10 (0.21)
Mn	0.05 (0.01)	0.04 (0.01)	0.05 (0.01)	0.04 (0.01)
Mg	2.11 (0.06)	1.63 (0.03)	2.11 (0.09)	1.75 (0.06)
Ca	0.65 (0.02)	0.70 (0.02)	0.62 (0.05)	0.62 (0.02)
Na	1.02 (0.07)	1.44 (0.04)	0.96 (0.07)	1.03 (0.06)
K	1.65 (0.09)	1.65 (0.09)	1.74 (0.12)	1.57 (0.19)
P	0.13 (0.02)	0.03 (0.01)	0.11 (0.01)	0.08 (0.06)

bloom predictably occurs during prolonged salinity stratification (Cloern, 1984), correlations between these variables are not surprising. Thus, a regression approach cannot positively identify controlling mechanisms for trace metal distributions, but may serve as a useful exploratory tool to examine processes potentially significant among cruises.

The positive correlation of DOC and SAL with dissolved Cu and dissolved Zn raises the possibility that Cu and Zn are predominantly associated with SAL-dependent dissolved organic matter in the South Bay water column (Figure 4). Previous studies have determined the presence and certain chemical properties of Cu-organic chelates in other estuarine environments (Sholkovitz & Copland, 1981; Mills *et al.*, 1982; Hanson & Quinn, 1983). DOC concentrations measured between 1979 and 1985 (Showalter, personal communication) also showed a positive correlation between dissolved metal and DOC concentrations near the mouth of the Guadalupe River (Figure 1), a major freshwater source to the South Bay.

Chemical simulations

Chemical speciation computations were employed to further examine the role of DOC in regulating metal speciation in the estuary. Using the computer program MINEQL (Westall *et al.*, 1976), Cu and Zn speciation in the South Bay were estimated using thermodynamic data of Mantoura *et al.* (1978) for dissolved organic complexation, and data of Hogfeldt (1983) for inorganic complexation. An exception was the constant for the formation of aqueous $\text{Cu}(\text{OH})_2$, $\log^*\beta_2 = -16.2$, that was taken from a study that closely examined both inorganic and organic complexation of Cu (Sunda & Hanson, 1979).

A 3 : 1 ratio of seawater to riverine water [i.e. calculated mean salinity = 0.027, ionic strength (I) = 0.5 M] was assumed for determining major ion concentrations. End member concentrations for major ions in seawater and the Guadalupe River were taken from Brewer (1975) and Anderson *et al.* (1983), respectively. Activity coefficients for inorganic complexation were calculated using the Davies equation (Westall *et al.*, 1976). Seawater stability constants for dissolved organic complexation (Mantoura *et al.*, 1978) were used directly. Other fixed parameters for this calculation were: (1) pH 8 compared to an observed range of 7.6 to 8.2, (2) typical dissolved Cu and Zn concentrations of $3 \mu\text{g l}^{-1}$ (c. 50 nM), (3) a $1.2 \mu\text{M}$ concentration of dissolved organic ligand sites, based on measured humic substance concentrations and corresponding to 10^{-6} moles binding sites per mg-C in the humic substance (Mantoura & Riley, 1975; McKnight *et al.*, 1983; Davis, 1984).

Chemical equilibrium computations indicate that sites on humic materials should be primarily bound to Mg, but c. 80% of the dissolved Cu would also be organically complexed. An alternative two-site binding model proposed by McKnight and Wershaw (1989) for Cu-organic complexation results in >90% of the total Cu complexed. Because the formation constants for Zn-humate complexes are typically orders of magnitude lower than for Cu-humate complexes (Mantoura *et al.*, 1978; van den Berg *et al.*, 1986), the calculation for Zn indicates that its speciation is controlled by inorganic complexation (primarily with chloride) with <10% of the dissolved Zn organically complexed. So although dissolved Zn concentrations correlated with DOC, our calculations do not indicate control of Zn speciation by organic complexation.

Limitations to the above metal speciation calculations bear close examination. First, chemical reactions with suspended particle surfaces were not considered in this computation. This limitation may have ecological implications, in that particle-bound

metal may increase metal bioavailability under conditions favorable for metal desorption (Kuwabara et al., 1986).

Second, other values for $\log^*\beta_2$, the constant for the second hydrolysis equilibrium for Cu, have been reported and generally range between -13.7 and -17.3 (Vuceta & Morgan, 1977). Both of these $\log^*\beta_2$ values have little effect on Cu speciation with $>90\%$ of the total Cu still organically complexed. Computed Zn speciation was not discernably affected by these changes in the $\log^*\beta_2$ value for Cu. Similarly, a change of pH in our computation to either 7.6 or 8.2 (the lowest and highest measured value for our sampling period) does not alter the result that $>90\%$ and $<5\%$ of the dissolved Cu and dissolved Zn, respectively, are organically complexed.

Third, although the water column of San Francisco Bay is well-oxygenated (Smith & Herndon, 1980), dissolved sulfide could be present due to slow oxidation of sulfide diffusing from the bottom sediment. Speciation calculations suggest that over the range of sulfide concentrations observed by Vivit et al. (1984) during a drought year in the South Bay ($0.1\text{--}3.2 \times 10^{-7}$ M total sulfide), metal sulfide interactions could be important during times of high dissolved sulfide concentrations, but probably not important at lower concentrations.

Finally, variability in the chemical character of the dissolved organic matter could affect the applicability of the formation constants used here. McKnight et al. (1983) found that Cu associated with fulvic acids from 17 aquatic environments throughout the United States could be consistently modeled by two formation constants (i.e. for strong and weaker binding sites). Van den Berg et al. (1987) have, however, reported higher log stability constants for Cu-humate and Zn-humate complexes in the Scheldt Estuary of c. 14 and 10, respectively. If these higher constants were used in our computations for the South Bay, both Zn and Cu speciation would be dominated by complexation with DOM. However, the log stability constants used in our calculations are conservative estimates relative to the range of published values and, in addition, do not reflect the potential for additional metal binding to dissolved organic material not efficiently isolated by conventional methods like XAD-8 extraction. Ionic strength corrections were not made to the formation constants for metal-organic complexation due to a lack of thermodynamic data. At pH 8 the ionic strength effect is probably not pronounced due to conformational changes in the humic substances and because of additional complexation of hydrolyzed metal species by organic ligands (Cabaniss & Shuman, 1987). A conventional Davies correction, for example, would greatly over estimate the ionic strength effect on metal-EDTA formation constants (Anderegg, 1977). In summary, dissolved Cu is quite likely associated with DOM, except possibly during periods when dissolved sulfide is elevated in the water column. Correlation between Cu, DOC and SAL raises the possibility that organically bound Cu is transported through the South Bay without significant net interaction with particles. Zn association with DOC is supported only if relatively high formation constants like those reported by van den Berg et al. (1987) are employed. However, the potential importance of such complexation cannot be excluded because of the observed Zn, DOC and SAL correlations.

Ecological implications

It has been well-demonstrated that the chemical speciation of Cu and Zn significantly affects the bioavailability of these metals to phytoplankton (Sunda & Guillard, 1976; Anderson et al., 1978), and that submicromolar activities of these metals can cause toxic effects on various algal species (Gavis et al., 1981; Anderson et al., 1978; Kuwabara, 1981).

Estimates for Cu, Zn and Cd free ion activities computed from our chemical simulation are of the order of 10^{-10} , 10^{-8} and 10^{-10} M, and are similar to threshold toxicity concentrations determined in the studies cited above. Using bacterial bioassays, Sunda (1987) estimated similar activity for the free cupric ion at similar total Cu in the marine plume of the Mississippi River.

The phytoplankton community structure in South San Francisco Bay is dominated by diatoms and small flagellates including cryptophytes (Wong & Cloern, 1981, 1982); dinoflagellates are rare. Phytoplankton communities in many other estuarine environments including Tomales Bay, a pristine estuary in close proximity to San Francisco Bay, are at least periodically dominated by dinoflagellates (Graneli et al., 1986; Cole, personal communication). Evidence exists that elevated free metal ion activities favor the dominance of diatoms over dinoflagellates (Mandelli, 1969; Brand et al., 1986). Brand et al. (1986) found that Cu free ion activities between $10^{-10.4}$ and $10^{-11.1}$ M caused 50% inhibition of reproductive rates in four species of neritic dinoflagellates, while similar growth inhibition of eight neritic diatoms was observed between $10^{-9.5}$ and $10^{-10.5}$ M free Cu ion activity. Differences in Cd sensitivity between neritic dinoflagellates and diatoms were less pronounced, with 50% growth inhibition for dinoflagellates observed between $10^{-8.7}$ and $10^{-9.6}$ M free Cd ion activity versus a range of $10^{-8.1}$ and $10^{-9.4}$ M for diatoms. The order of magnitude of the free metal ion activities estimated for South San Francisco Bay combined with the small contribution of dinoflagellates to the phytoplankton community, raise the possibility that elevated free metal ion activities affect the phytoplankton community structure in favor of metal-tolerant species in the estuary.

Reactions with particles

As a rule, our dissolved trace metal data do not show large deviation from a linear fit of metal concentration to salinity. Thus, trace metal removal is not detectable, except possibly with Cu during the final September cruise (Figure 3b). On that date SPM was the highest observed in the study and Cu concentrations were the lowest (lower than suggested from the relationship with DOC) (Table 1, Figure 4a). In the Tamar Estuary, suspended particulate loads of 200 mg l^{-1} and salinities of <0.005 were accompanied by removal of dissolved Cu, Zn and Mn (Ackroyd et al., 1986). Although these suspended loads and salinities are well outside the range of values observed in this study, they demonstrate that removal of metals from the dissolved phase by adsorption is feasible when suspended particulate loads are high (Morris, 1986; Ackroyd et al., 1986). The apparent removal from solution at Station 36 was more pronounced for Cu than for Zn during the September cruise in the present study (Figure 2a and 2b). This observation is consistent with work by Mouvet and Bourg (1983), who showed that Cu has a greater affinity than Zn or Cd for adsorption sites on River Meuse bottom sediments (surface constants of $10^{-1.8}$, $10^{-3.6}$, $10^{-3.7}$ for Cu, Zn and Cd, respectively).

In May 1984 (a dry year when an algal bloom was not detected in the South Bay), high dissolved Cu (14×10^{-8} M) at Station 36 accompanied high SPM (22 mg l^{-1}), but DOC (4.5 mg l^{-1}) concentrations were nearly twice those in September 1985. The interaction of Cu, DOC and particulate material is apparently complex in San Francisco Bay and may be characterized by some annual variability in the relative importance of processes affecting Cu speciation and distribution.

Partitioning coefficients for all three trace metals decreased with increased salinity. This trend is consistent with previous laboratory and field experiments (Van de Meent et al., 1985). In laboratory experiments using iron hydroxides, trace metal adsorption is

typically shifted to higher pH with increased chloride concentration (Davis & Leckie, 1978; Millward, 1980; Millward & Moore, 1982). This general behaviour has been attributed to changes in metal speciation due to chloro-complex formation (particularly for Cd) and increased competition by major cations in the seawater matrix for adsorption sites.

An alternative explanation for the observed decrease in K_D with salinity would be a physical mixing of marine particles, characterized by a low K_D , with estuarine particles associated with a higher K_D . The inorganic composition of the suspended sediment does not vary greatly (Table 4), but the organic character of the particles do differ within the Bay (Table 1). In fact, elevated particulate organic carbon and chlorophyll-a, a measure of phytoplankton biomass, were associated with elevated K_D values and lower salinities (Table 2). The importance of metal association with particle-bound organic matter has been well established in previous studies (Davis, 1984; Di Giulio & Scanlon, 1985).

In modeling the effect of POC on trace metal sorption, others have estimated POC concentrations assuming that the relationship between POC and the ratio of DOC to SPM is linear (Mouvet & Bourg, 1983). The rationale for this assumption is that a scarcity of adsorption sites induces higher POC values at low SPM concentrations. This assumption is not appropriate for the South Bay. Even if the March data are omitted from the regression (the only sample date when phytoplankton constitute a significant POC fraction), the ratio of DOC to SPM explains only 9% of the total POC variance.

Cadmium

The distribution of dissolved Cd, relative to Cu and Zn, depicts a more complex relationship with: (1) a relatively weak dependence on salinity (Table 2); (2) a positive correlation with SPM; and (3) less dissolved Cd with the presence of elevated POC (Figure 5). The correlation with SPM suggests that the suspended sediment could serve as a source of dissolved Cd if Cd associated with suspended particles is redistributed into solution as the particles enter high salinity bay waters. Although, there could be undefined sources of dissolved Cd coincident with SPM concentrations (i.e. runoff), the possibility of Cd desorption from SPM in the South Bay is also supported by the observed decrease in particulate Cd with increased salinity (Table 1). In the Amazon Plume, Boyle *et al.* (1982) observed evidence of Cd desorption from suspended sediment. Total Cd (dissolved and suspended) was <0.1 nM, i.e. an order of magnitude less than concentrations observed here. Laboratory observations show that Cd adsorption is depressed with increased salinity (Salomons, 1980). Cd desorption is enhanced by CdCl^+ and CdCl_2 formation, which are less likely to adsorb than Cd^{+2} (Benjamin & Leckie, 1982), and to Mg competition for Cd adsorption sites (Balistriero & Murray, 1982), all of which occur as particles with adsorbed Cd move from freshwater into the Bay.

When particles were rich in POC in March 1985, less Cd was observed in solution than expected from measured SPM (Figure 5). Enhanced Cd adsorption onto amorphous iron hydroxide in the presence of humic substances has been previously observed in laboratory experiments (Laxen, 1985) under conditions of low total iron (c. 10^{-5} M). Others, however, have found that this affinity of Cd for POC is less significant under conditions of higher inorganic adsorption site densities (Davies-Colley *et al.*, 1984; Davis, 1984). Ten-fold higher Cd partitioning coefficients in the Western Scheldt Estuary compared to the South Bay (POC concentration ranges of 1.3 to 5.5 mg l^{-1} and 0.2 to 1.9 mg l^{-1} , respectively) also are consistent with the notion of a Cd-POC association (Valenta *et al.*,

1986). This difference resulted from order of magnitude higher particulate Cd concentrations in the Western Scheldt relative to the South Bay (dissolved Cd concentrations were similar).

Although riverine sources represent a major freshwater input to the South Bay during the winter and spring (when virtually all precipitation for the year occurs), the major freshwater source to the South Bay during the summer dry season is effluent from municipal treatment plants (Table 1). With effluent concentration ranges for total Cu, Zn and Cd of 30 to 280 nM, 150 to 960 nM and c. 20 nM, respectively, treatment plant effluent represented a significant trace metal input to the South Bay during our sampling period. If the consistent correlations for dissolved Cd with SPM and dissolved Cu with DOC reflect geochemical associations, then the chemical character of the SPM and DOC may not have varied greatly over the spatial and temporal range of the sampling (despite large changes in the sources of freshwater). Major elemental analyses of the suspended sediment collected during subsequent cruises, and humic substance extractions of dissolved organic carbon, tend to support this hypothesis (Tables 3 and 4). Furthermore, X-ray diffraction of suspended sediment from these cruises indicates very similar mineralogy with samples dominated by illite and smaller amounts of quartz and chlorite.

It is clear from the previous discussion that many processes that affect trace metal distributions in South San Francisco Bay also operate in other estuaries. However, observations contrary to those discussed here have also been noted. For example, Villa and Pucci (1987), working in the anthropogenically-affected Blanca Bay, observed a positive correlation between dissolved Cd and POC and no correlation between dissolved Cd and SPM. Dissolved Zn was not significantly correlated with any of their measured parameters. Wangersky (1986) asserted that the principal routes of trace metal removal from solution in surface waters are physical and biological rather than strictly chemical. He based this statement on a review of the importance of chemical interactions of trace metals with dissolved and particulate organic matter, as well as biologically-mediated chemical reactions. In attempting to understand and predict trace metal behavior in aqueous environments, investigators should be wary of searching for generic answers to explain trends from one study site to another. Rather, a spatial and temporal description of the interdependence of chemical, physical and biological processes, unique to each system, is ultimately required.

Conclusions

Trace metal distributions in the water column were observed during and after a spring phytoplankton bloom in South San Francisco Bay. Strong positive correlations between dissolved Cu and DOC, and dissolved Zn and DOC, were observed. Control of Cu speciation by metal-humic material complexation in this part of the estuary is a process consistent with available elemental and thermodynamic data. However, analogous controls for Zn were not indicated by the speciation calculations. These computations also indicate that elevated free metal ion activities may be among the factors that control growth of certain phytoplankton species within the South Bay. Both Cu and Zn were significantly partitioned in solid and solution phases, whereas Cd was present primarily in solution. Results suggest a source for dissolved Cd coincident with elevated SPM. Interdependent processes that control the distribution of these metals were apparently element specific, but for the most part consistent over the temporal and spatial scales of this study.

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