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Metal uptake by phytoplankton during a bloom in South San Francisco Bay: Implications for metal cycling in estuaries

Abstract—The 1994 spring phytoplankton bloom in South San Francisco Bay caused substantial reductions in concentrations of dissolved Cd, Ni, and Zn, but not Cu. We estimate that the equivalent of ~60% of the total annual input of Cd, Ni, and Zn from local waste-water treatment plants is cycled through the phytoplankton in South Bay. The results suggest that processes that affect phytoplankton bloom frequency or intensity in estuaries (e.g. nutrient enrichment) may also affect metal trapping. The bloom was characterized by hydrographic surveys conducted at weekly intervals for 9 weeks. Metal samples were collected from the water column on three occasions, timed to bracket the period when the bloom was predicted. Factors that might confound observations of biological influences, such as freshwater inputs, were relatively constant during the study. Before the bloom, concentrations of dissolved Cd were 0.81 ± 0.02 nmol kg^{-1}, Zn concentrations were 19.8 ± 1.5 nmol kg^{-1}, Ni were 42 ± 1.4 nmol kg^{-1}, and Cu were 37 ± 1.4 nmol kg^{-1}. These values are elevated relative to riverine and coastal end-members, reflecting inputs from wastewater and(or) sediments. At the height of the bloom, dissolved Zn, Cd, and Ni were reduced to 19, 50, and 75% of their prebloom concentrations, respectively. Dissolved Cu concentrations increased 20%. The mass of Cd taken up by phytoplankton was similar to the mass of Cd removed from solution if particle settling was considered, and Cd concentrations estimated in phytoplankton were higher than concentrations in suspended particulate material (SPM). Particulate concentrations of Zn and Ni during the bloom appeared to be dominated by the influence of changes in resuspension of Zn- and Ni-rich sediments.

Trace metal concentrations in many of the world's estuaries are enriched as a result of industrialization and human development in the coastal zone (Windom et al. 1989; Fowler 1990). The ecological significance of metal enrichment can be difficult to determine because important aspects of metal cycling are not fully understood. For example, the role of phytoplankton blooms as biological agents of geochemical variability in estuaries is now clearly established for nutrients (e.g. Cloern 1996), but is not well known for metals. In oceans, vertical profiles of some dissolved metals follow the profiles of nutrients, suggesting similarities in biologically driven cycling (Bruland 1980, 1983). In some instances depletion of dissolved trace elements in oceans and lakes also coincides with increased phytoplankton production (Wrench and Measures 1982; Wangersky 1986; Reynolds and Hamilton-Taylor 1992; Kremlin and Pool 1989; Rico et al. 1993). Experimental studies in large enclosures show that phytoplankton blooms can remove metals from solution (Slauenwhite and Wangersky 1991; Apte et al. 1986). However, in estuaries, direct linkages between primary production and metal dynamics often may be masked because of the complexity of inputs and physicochemical processes (Sigg 1985; Murray 1987). Sharp et al. (1984) were able to observe a coincident decline in dissolved phosphate and dissolved Cd in association with a phytoplankton bloom in the Delaware Bay, but such observations are rare.

The present study was designed to exploit the predictability of the spring phytoplankton bloom in South San Francisco Bay (Cloern 1996). The influence of phytoplankton uptake (defined here as both sorption onto cell surfaces and incorporation into cells) on the cycling of Cd, Cu, Ni, and Zn during the 1994 spring bloom was examined. The objectives were to determine (1) if phytoplankton are important in scavenging and cycling of trace elements in an estuary, (2) whether the importance of biogeochemical transformation differs among metals, and (3) what proportion of the anthropogenic metal input to San Francisco Bay cycles through this pathway.

South San Francisco Bay (South Bay) is a coastal embayment with large expanses <2 m deep and a narrow central channel with a mean depth of ~10 m. Freshwater inputs from precipitation and river inflows reduce salinities to 20–25 psu during the well-defined wet season, which occurs between January and May (Conomos 1979). Local freshwater inputs from municipal wastewater treatment plants and

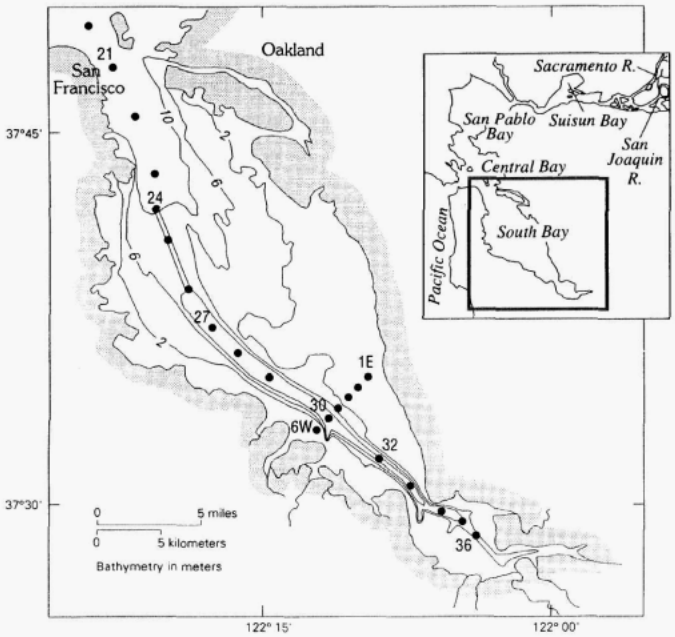


Fig. 1. Map of South San Francisco Bay showing sampling sites for the hydrographic surveys and the metals transect.

runoff from the densely populated urban watershed deliver sediment, nutrients, and contaminants, including metals. Metal concentrations in South Bay are much higher than in the adjacent coastal ocean or in freshwater end-members (Flegal et al. 1991; van Geen and Luoma 1993) as a result of inputs from waste waters and(or) bottom sediments (Flegal et al. 1991).

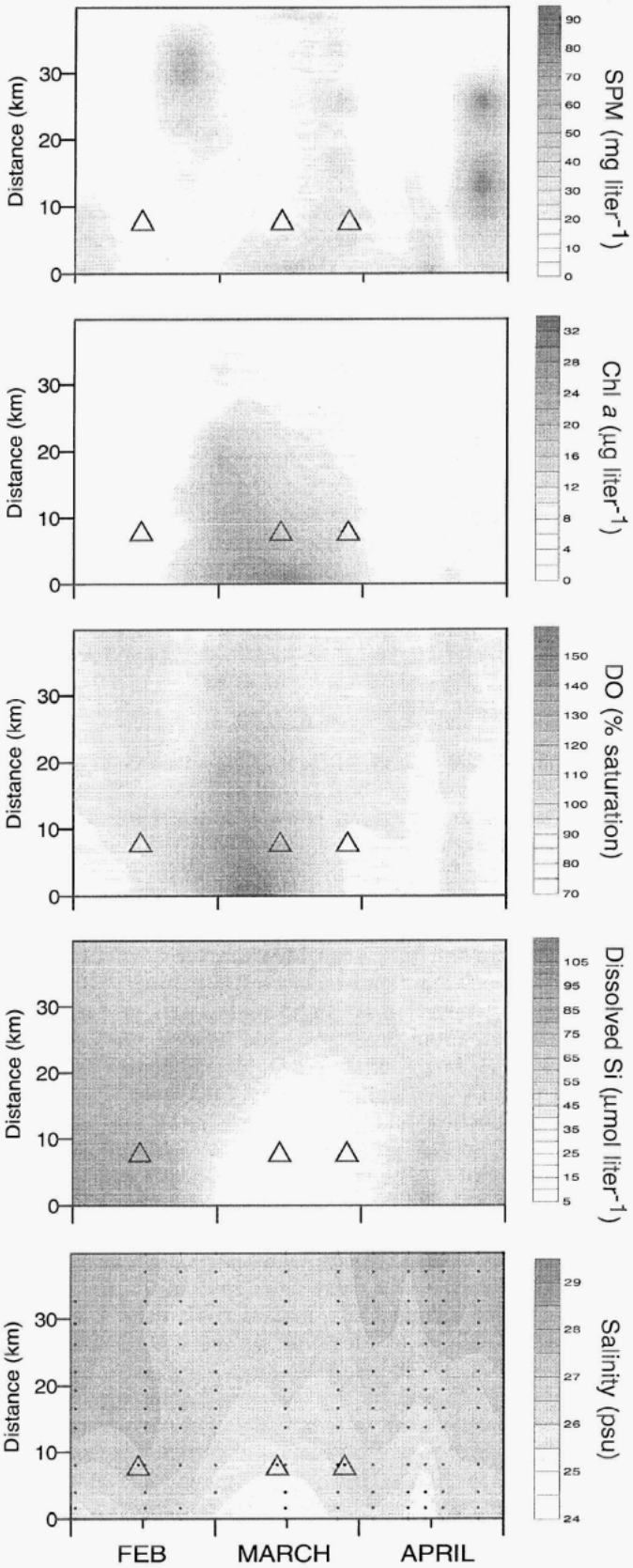
Phytoplankton dynamics are dominated by a spring bloom that occurs during February–May, usually as a series of sequential biomass fluctuations that are typically composed of coastal diatom species (e.g. *Skeletonema costatum, Thalassiosira* spp., *Leptocylindricus danicus, Coscinodiscus* spp., *Ditylum brightwelii*). The timing of the bloom is somewhat predictable because it usually occurs during the neap-tide periods of reduced vertical mixing (Cloern 1996). Typically, Chl *a* concentrations increase from a baseline of 1–2 μg liter^{-1} to peaks of 40–60 μg liter^{-1} during the spring bloom, although the magnitude fluctuates from year to year with differences in hydrology, weather patterns, and trophic interactions (Cloern 1996).

To characterize the 1994 bloom, hydrographic surveys were conducted weekly between 2 February and 27 April 1994. During this period, vertical profiles of the water column were conducted on 11 occasions at 13 stations along a 40-km north–south longitudinal transect between the Dumbarton Bridge (USGS Sta. 33) and the San Francisco–Oakland Bay Bridge (USGS Sta. 21) (Fig. 1). The instrument package used for the hydrographic profiles consisted of Seabird Electronics (SBE) CTD sensors, SeaTech fluorometer, SBE optical backscatter sensor (OBS), and SBE oxygen electrode. The oxygen electrode, fluorometer, and OBS were calibrated each cruise with ~12 discrete analyses for dissolved oxygen (high-precision Winkler titration following Granéli and Granéli 1991), Chl *a* concentration (spectrophotometric determination from acetone extracts of samples collected onto GF A/E filters; Lorenzen 1967), and concentration of suspended particulate matter (gravimetric determination of samples collected onto 0.4-μm Nuclepore filters; Hager 1993). Edmunds et al. (1995) gave detailed methods and results of this measurement program. Nutrient concentrations were also measured in surface waters along the longitudinal transect (Hager 1997). Buchanan et al. (1996) and Schoellhamer (1996) determined resuspension continuously in subsurface waters from optical backscatter sensors moored on the San Mateo Bridge, near USGS Sta. 29 (Fig. 1), 1 and 7.5 m above the bottom of the ship channel, north of the trace metal transect.

Samples were collected for analysis of dissolved and particulate metals along an east–west transect centered at USGS Sta. 30 (Fig. 1) on three dates in 1994: 15 February before the bloom began, 15 March in midbloom, and 29 March toward the end of the bloom. On each date six samples were collected at ~1-km intervals along the transect, transverse to the channel across the subtidal shallows.

Nutrients, suspended particulate material (SPM), and salinities were analyzed with the metals in each water sample. Samples were collected in acid-washed polyethylene bottles from the bow of a slowly moving small boat and were stored in the dark until filtration at the end of the day in the laboratory. Filtrations were conducted under a class 100 laminar flow bench using an acid-washed 0.4-μm Nuclepore filters in an acid-washed polycarbonate filtration system adapted for vacuum filtration and equipped with a Teflon O-ring. Filtered trace metal samples were acidified with 0.5 mL 12 N Ultrex II HCl per 250-ml sample. Nutrient samples were filtered through disposable 0.45-μm Durapore filters and acidified with 60 μl of 12 N Ultrex II HCl per 60 ml of seawater. Dissolved silicate and phosphate were measured by spectrophotometry with a Lachat Quickchem AE flow-injection system. Salinity was measured on subsamples stored in glass using a salinometer standardized with IAPSO water. Preconcentration and analytical techniques for dissolved metal analyses were those described by van Geen and Husby (1996).

The particles collected on the 0.4-μm Nuclepore filters were dried in the class 100 laminar flow hood. The dry weight of the particles was measured gravimetrically with salt weight correction by analyses of Na content. The mean filter weight was determined from several unused filters within each batch; the average filter weight was 15.6 $\pm$ 1 mg. The filters with particles were placed in 15-ml Teflon vessels with 3 ml of an Aqua regia mixture of 3 parts 12 N Ultrex HCl to 1 part 16 N Ultrex HNO_3 for partial (near-total) decomposition. The vessel was sealed and the samples were refluxed at 95°C for 12 h in an aluminum heating block that heated the samples at even temperature. The samples were then evaporated to near dryness in a clean hood, reconstituted in 3 ml of 0.6 N Ultrex HCl, centrifuged to remove residual particles, and transferred to acid-cleaned centrifuge tubes until analysis. Concentrations of Cd, Cu, Ni, and Zn were analyzed by graphite furnace atomic absorption spectrophotometry (GFAAS) with calibration by standard additions. Aluminum and Na concentrations were determined by flame atomic absorption spectrophotometry. Pro-



cedural blanks were all <10% of lowest concentrations determined. Estuarine sediment (NBS 1646) was digested along with the samples and analyzed as standard reference material. More than 95% of the certified Cd and Ni was recovered, and >85% of Cu and Zn was recovered. Aluminum recoveries were 58%. No attempt was made to correct the concentrations for less than full recovery. Al values will be expressed as leachable Al.

The 1994 spring bloom was a month-long event of high phytoplankton biomass with a mesoscale spatial pattern typical for South Bay (Cloern 1996). Peak Chl *a* (~50 μg liter^{-1}) was observed landward in the southernmost reach of the estuary, and there was a persistent gradient of decreasing Chl *a* concentration in the seaward direction (Fig. 2). Primary productivity was not measured directly, but dissolved oxygen concentration is a useful surrogate. Oxygen content of near-surface waters is undersaturated with respect to atmospheric oxygen, except during blooms when the rate of photosynthesis accelerates and leads to supersaturation (Cloern 1996). The weekly determinations of oxygen indicated that the highest primary productivity occurred in early March in the southernmost reach (30 km from the mouth), adjacent to the metal transect (Fig. 2). On 9 March the highest dissolved oxygen concentrations were >150% supersaturated.

Surface salinities are an indicator of the variability of freshwater input and thus of delivery of nutrients (and probably metals) from freshwater sources (Flegal et al. 1991; Hager 1993). The full range of salinity variation was 24.1 to 29.1 psu throughout South Bay during February and March 1994 (Fig. 2). Salinities also varied little (25.6–26.4 psu) along the transverse transect among the sampling dates. The relatively small variability in salinity indicated that changes in inputs of metals were probably small during the study period.

Changes in suspended particulate matter concentrations during the measurement period (Fig. 2) were linked to changes in semidiurnal tides, neap-spring tidal fluctuations, and resuspension by wind events (Schoellhamer 1996). SPM increased in surface waters along the entire north–south axis of South Bay on 29 March (Fig. 2) because of a spring tide. An episode of increased resuspension was also measured by the subsurface OBS monitors on 15 March (Buchanan et al. 1996), which was reflected in elevated SPM concentrations at the shallow-water metal transect stations on 15 March, but not at the deeper channel station.

Surface concentrations of nutrients (silicate, phosphate,

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Fig. 2. Hydrographic variability around the 1994 spring bloom in South San Francisco Bay showing spatial–temporal distributions of SPM (top panel), Chl *a*, dissolved oxygen, dissolved silicate, and salinity (bottom panel). The gray-scale contours were drawn from interpolation (kriging) of near-surface measurements made along the longitudinal transect from channel Sta. 33 (kilometer 0) to Sta. 21 (kilometer 39.8; Fig. 1) on 11 dates between 2 February and 27 April. Sampling points are shown as filled circles in the lower panel. The open triangles show the times and position of the transverse transect for trace metal sampling.

Table 1. Concentrations of dissolved metals, silicate, and phosphate at a six-site transect in South San Francisco Bay on three dates in 1994: before the phytoplankton bloom (15 February), mid-bloom (15 March), and as the bloom receded (29 March). Site numbers decline from west to east in the transect. Sta. 5Ch was in the channel; other stations were in more shallow waters.

Sta.	PO_4^{3-} (μmol liter^{-1})	Si	Cd	Cu	Ni	Zn
		nmol kg^{-1}				
			15 Feb			
6W	8.9	104	0.81	34	40	20
5Ch	10.1	113	0.84	38	43	22
4	9.3	104	0.78	36	41	17
3	9.8	104	0.81	37	42	20
2	10.0	101	0.80	38	43	20
1E	9.9	96	0.80	38	44	20
Mean	9.7	104	0.81	37	42	20
SD	0.4	5	0.02	1	1	1
			15 Mar			
6W	4.1	8.9	0.47	42	43	4.7
5Ch	5.2	6.9	0.42	45	31	4.6
4	4.3	2.9	0.38	44	30	2.9
3	3.9	5.4	0.41	43	29	4.6
2	4.1	1.3	0.36	47	29	2.5
1E	4.3	1.4	0.36	50	31	3.4
Mean	4.3	4.5	0.40	45	32	3.8
SD	0.4	2.8	0.04	3	5	0.9
			29 Mar			
6W	7.5	29	0.54	50	38	7.2
5Ch	7.2	28	0.53	49	34	4.7
4	7.3	27	0.51	51	36	6.0
3	5.7	19	0.47	46	30	3.5
2	5.9	21	0.48	47	31	3.4
1E	5.3	8.5	0.46	50	30	2.8
Mean	6.5	22	0.50	49	33	4.6
SD	0.9	7	0.03	2	3	1.6

nitrate) were depleted over a substantial area of the South Bay near the peak of the bloom on 15 March (Si shown in Fig. 2). Near-surface nitrate concentrations in the lower estuary dropped from a range of 40–80 μmol liter^{-1} on 17 February to 4–23 μmol liter^{-1} on 9 March (Hager 1997). The strong depletion of dissolved silicate (Fig. 2) reflected the dominance of the bloom by diatoms. Concentrations of dissolved Si were >100 μmol liter^{-1} before the bloom began. As the bloom developed and diatoms removed Si from solution, concentrations fell to 5 μmol liter^{-1} in the area of most intense primary production adjacent to the metal transect. Overall, depletion of Si was widespread in South Bay.

Nutrient (Si and PO_4^{3-}) depletion in the metal samples was similar to that observed in the broader surveys (Table 1, Fig. 3). For example, Si concentrations averaged 104 $\pm$ 6 μmol liter^{-1} on 15 February, 5 $\pm$ 2 μmol liter^{-1} on 15 March, and recovered to 22.4 $\pm$ 6 μmol liter^{-1} on 29 March. Phosphate was 9.7 $\pm$ 1 μmol liter^{-1} on 15 February, declined to 4.3 $\pm$ 0.5 μmol liter^{-1} on 15 March during the bloom, and was 6.5 $\pm$ 1 μmol liter^{-1} on 29 March. East-to-west variability was small compared to temporal variability.

Dissolved Zn, Cd, and Ni were significantly depleted on 15 March compared to 15 February, but Cu was not (Table 1, Fig. 3). Dissolved Zn concentrations, averaged across the transect on 15 March, were 19% of the values on 15 February. Cadmium concentrations declined to 50% of their original value and Ni concentrations to 75%. All these differences were statistically significant ($P < 0.05$; t-test for paired values). Dissolved Zn and Cd increased between 15 and 29 March, but did not return to their February values. In contrast to the other metals, dissolved Cu concentrations increased ~20% in March (Fig. 3).

The parallel occurrence of metal and nutrient (Si and P) depletion in the metal transect between 15 February and 15 March 1994, coupled with the broad depletion of Si observed in the hydrographic survey, suggested that metal and nutrient depletion by phytoplankton occurred throughout South Bay. Metal and nutrient dynamics are influenced by multiple sources, sinks, and transformations, but the large depletions of dissolved Ni, Cd, Zn, Si, and P during the bloom development suggest that algal uptake was the dominant process of variability then. Depletion of Si can be highly variable and community dependent in a bloom. Therefore, the metal and P data from the period of depletion were used to estimate the significance of phytoplankton metal uptake. We can estimate the ratios of metal and phosphorus incorporation into phytoplankton biomass as

$$\gamma_M = \Delta M/\Delta \mathrm{P}, \tag{1}$$

where ΔM is the change in mean concentration of dissolved metal M between 15 February and 15 March (Table 1), and ΔP is the change in mean phosphate concentration during that same period.

From metal : P stoichiometries we can estimate the annual phytoplankton uptake of dissolved metals by multiplying the γ_M ratios times the total mass of phosphorus assimilated by the phytoplankton in a year. Measurements of net primary production in South San Francisco Bay during 1980 showed that annual production is ~12.5 mol C m^{-2} yr^{-1} (Cole and Cloern 1984). From this result, and using a surface area of 5.5×10^8 m^2 (Jassby et al. 1993), we calculate a South Bay annual primary production of 6.9×10^9 mol C yr^{-1}. This carbon production is equivalent to a phosphate uptake of ~6.5×10^7 mol P yr^{-1}, assuming the Redfield ratio of 1 mol P : 106 mol C. The product of this annual P uptake times γ_M gives an estimate of the potential mass of each metal that can be taken up by the phytoplankton. We summarize these calculations in Table 2, along with comparisons to the annual loadings of each metal from municipal waste treatment facilities. On an annual basis, masses equivalent to ~60% of the waste loadings of these metals are cycled through the phytoplankton. These estimates have large uncertainties because they are based on the assumption that algal metal : P ratios are constant; this assumption might only be valid over a small range of dissolved metal concentrations (e.g. Sunda and Huntsman 1992). However, the magnitude of these estimates suggests that algal uptake is a prominent mechanism of metal cycling in this estuary.

In the open ocean, the vertical distributions of Cd and Zn are closely correlated to the distribution of the nutrients phosphate and silicate, respectively (Bruland 1980). The corresponding slopes of the near-linear oceanic relationships in-

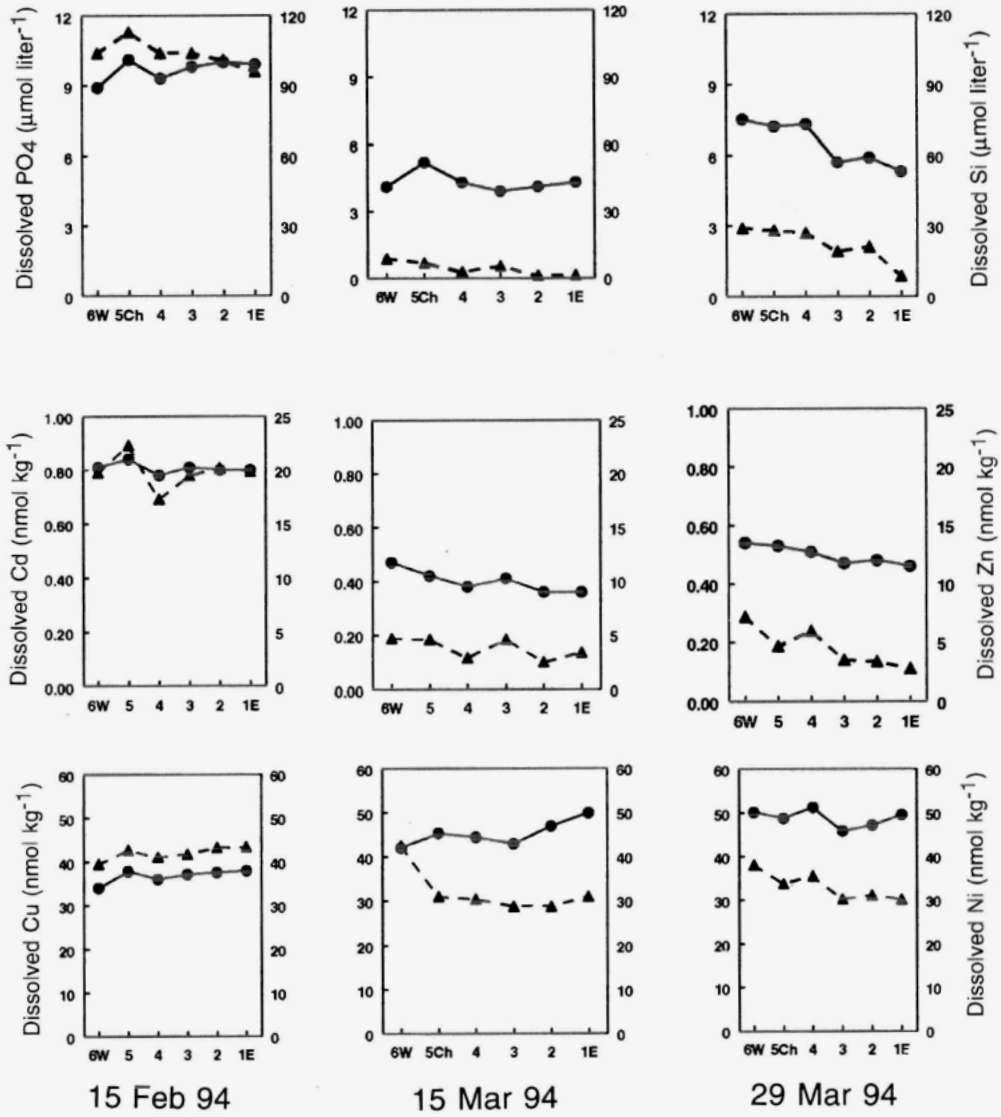

Fig. 3. Dissolved concentrations of phosphate (●) and silicate (▲), cadmium (●), zinc (▲), copper (●), and nickel (▲) observed in samples collected in a transverse east (E)–west (W) transect in South San Francisco Bay on 15 February (before phytoplankton bloom), 15 March (midbloom), and 29 March (as the bloom receded). 5Ch is the station in the channel.

dicate that the mean composition of oceanic plankton is 34 $\times 10^{-5}$ mol Cd mol P^{-1} and 5.4 $\times 10^{-5}$ mol Zn mol Si^{-1}. The mean composition of South Bay plankton determined from a regression of the parallel bloom depletions was 7.6 $\times 10^{-5}$ mol Cd mol P^{-1} and 17 $\times 10^{-5}$ mol Zn mol Si^{-1}. Bay plankton were depleted in Cd relative to P (or were at the low end of all reported values; Bruland et al. 1991) and enriched in Zn relative to Si, when compared to oceanic plankton. In later work, Bruland et al. (1991) reported mol Ni : mol P of 21–35 $\times 10^{-5}$ in the North Pacific, compared to 300 $\times 10^{-5}$ in the Bay. Bay plankton appear to be substantially enriched in Ni. Lee et al. (1995) recently demonstrated that Cd functions as a nutrient for marine diatoms in typically Zn-limited open-ocean surface waters because Cd can substitute for Zn in carbonic anhydrase. It may be that the converse affects uptake in South Bay: reduced incorporation of Cd by Bay plankton reflects the availability of elevated levels of Zn in the water column. In making such simple comparisons, we must keep in mind the recent demonstrations that natural organic ligands can complex a large fraction of dissolved metals in the open ocean (Bruland et al. 1991) as well as in contaminated estuaries (Ahner et al. 1995). Antagonism for uptake by phytoplankton between Cu and Mn, Cu and Zn, Cd and Fe, and Mn and Zn, as reviewed by Sunda (1988–1989) and Bruland et al. (1991), could play a role in a metal-enriched estuary like San Francisco Bay. Laboratory experiments also indicate that ambient Cd : PO_4 ratios affect uptake (Kudo et al. 1996).

If dissolved metal depletion occurred solely via uptake into plant cells, then the net mass of metal taken up by phytoplankton during the bloom should balance the change in mass of dissolved metal. This can be difficult to demon-

Table 2. Potential phytoplankton uptake of Cd, Ni, and Zn in South San Francisco Bay, calculated from estimates of annual phytoplankton P uptake (6.5×10^7 mol P) and the ratios of metal (M): P incorporation into algal biomass, γ_M. Metal : P ratios were calculated from measured depletions during the 1994 spring bloom: ΔM is the change in mean concentration of metal M between 15 February and 15 March, and γ_M is the ratio of this depletion to the phosphate depletion (5.4 μmol P liter^{-1}). The estimated annual rates of algal uptake are compared to annual point-source loadings (Gunther et al. 1987).

	ΔM (nmol M kg^{-1})	γ_M (mol M : mol P)	Algal uptake (10^3 mol M yr^{-1})	Waste inputs (10^3 mol M yr^{-1})	% assimilated*
Cd	0.41	7.6×10^{-5}	4.9	8.3	59
Ni	10.0	1.85×10^{-3}	120	190	63
Zn	16.2	3.0×10^{-3}	195	310	63

* Percentage of annual inputs assimilated by phytoplankton.

strate in estuaries. Plant cells typically comprise a small proportion of the SPM and cannot be separated for specific analysis. Biogenic particles can sink rapidly in blooms dominated by diatoms (Smetacek 1985), and therefore the standing stock of plant biomass is not directly comparable to changes in dissolved metal. In addition, the particulate mass of metals in the water column or dissolved metal concentrations may be affected if sediment resuspension changes during the bloom.

Resuspension is an especially important consideration in a shallow estuary like South Bay. Concentrations of SPM, averaged across the metal transect, increased from 10.7 $\pm$ 2.9 mg liter^{-1} on 15 February to 27.3 $\pm$ 11.4 mg liter^{-1} on 15 March, when the bloom was at a maximum (Table 3). Increases in the suspended mass of leachable Al also occurred at every shallow-water transect station on 15 March (Table 3). Leachable Al concentrations are 1–3 mmol g^{-1} in the sediments of San Francisco Bay (Hornberger et al. in press), compared to 1–2 μmol Al g^{-1} in isolated algal cells (Bruland et al. 1991), so the increased mass of suspended Al was an indication that the sediment resuspension episode reported prior to 15 March (Buchanan et al. 1996) could have played a role in the changes in SPM concentrations.

The available biological data allow us to estimate the likely contribution of the bloom to the increase in SPM. Chl *a* concentrations were 23 μg liter^{-1} near Sta. 5Ch (as measured at Sta. 30 in the hydrographic survey) on 15 March. If phytoplankton biomass has 35 μg C per μg Chl *a* (Cloern et al. 1995) and C comprises 30% of the dry weight of diatom-dominated phytoplankton communities (Parsons et al. 1961), then the standing crop of phytoplankton on 15 March was

$$[(23\ \mu\text{g liter}^{-1}) \times (35\ \mu\text{g})]/0.3 = 2.7\ \text{mg liter}^{-1}. \quad (2)$$

Pheopigment determinations indicated that the contribution of phytodetritus from the bloom was similar to the measurable Chl *a* (data not shown). Therefore, the estimated total bloom-derived mass of suspended material was 5.4 mg liter^{-1}, a value not unusual for a South Bay bloom (Cloern 1996). This mass is ~20% of the total SPM of 27 mg liter^{-1}.

Table 3. Concentrations of SPM and particulate aluminum, cadmium, copper, nickel, and zinc in the water column at a six-site transect in South San Francisco Bay on three dates in 1994: before the phytoplankton bloom (15 February), midbloom (15 March), and as the bloom receded (29 March). Site numbers decline from west to east in the transect. Sta. 5Ch was in the channel; other stations were in more shallow waters.

Sta.	SPM (mg liter^{-1})	Al	Cd	Cu	Zn	Ni
		nmol liter^{-1}				
			15 Feb			
6	13.5	22.8	0.026	12.1	23	27
5Ch	15.0	28.1	0.029	14.7	27	32
4	6.6	8.7	0.020	6.2	11	15
3	9.2	13.7	0.030	8.1	17	16
2	8.8	10.9	0.020	6.7	12	13
1	11.1	13.7	0.022	7.7	20	19
Mean	10.7	16.3	0.025	9.3	18	20
SD	2.9	6.8	0.003	3.1	6	7
			15 Mar			
6	47.9	38.9	0.218	32.7	105	91
5Ch	8.8	9.6	0.054	5.6	13	15
4	24.8	21.7	0.135	23.8	53	56
3	24.5	21.6	0.101	19.0	54	58
2	28.9	19.7	0.132	20.1	51	50
1	28.8	20.8	0.127	18.3	46	46
Mean	27.3	22.0	0.128	19.9	54	23
SD	11.4	8.6	0.049	8.0	27	24
			29 Mar			
5Ch	12.3	13.3	0.034	8.4	13	24
4	20.4	19.6	0.079	16.6	27	44
3	16.7	7.3	0.043	10.0	15	21
2	27.2	38.6	0.072	23.8	38	52
1	21.8	25.6	0.084	17.2	29	47
Mean	19.7	20.9	0.062	15.2	25	38
SD	5.0	10.8	0.020	5.5	9	12

The change in total SPM averaged across the metal transect between 15 February and 15 March was ~16.6 mg liter^{-1}. If 5.4 mg liter^{-1} was bloom-derived, about one-third of this change originated from bloom material and two-thirds from resuspension. Multiplying ΔP (Eq. 1) by the Redfield ratio shows that 5.7×10^{-4} mol C liter^{-1} was produced during the bloom, which is 23 mg C liter^{-1}. If only 5.4 mg liter^{-1} of this was in suspension on 15 March, then 77% of the biogenic matter produced was removed by sinking and(or) filtering by the benthic macrofauna (Cloern 1982). Thus, the bloom accounted for 20% of the mass of the SPM present in the water column on 15 March and about one-third of the increase in SPM concentration between 15 February and 15 March. Only 23% of the total material produced by the bloom was in suspension on 15 March, however.

Understanding the bloom-derived contribution to the SPM allowed determination of the role of biogenic particle formation in the changes in particulate Cd. Before the bloom, the particulate load of Cd in the water column was much smaller than the dissolved load (Table 3, Fig. 4). During the bloom, dissolved Cd declined 0.40 nmol kg^{-1} but the standing stock of particulate Cd increased only 0.11 nmol liter^{-1}.

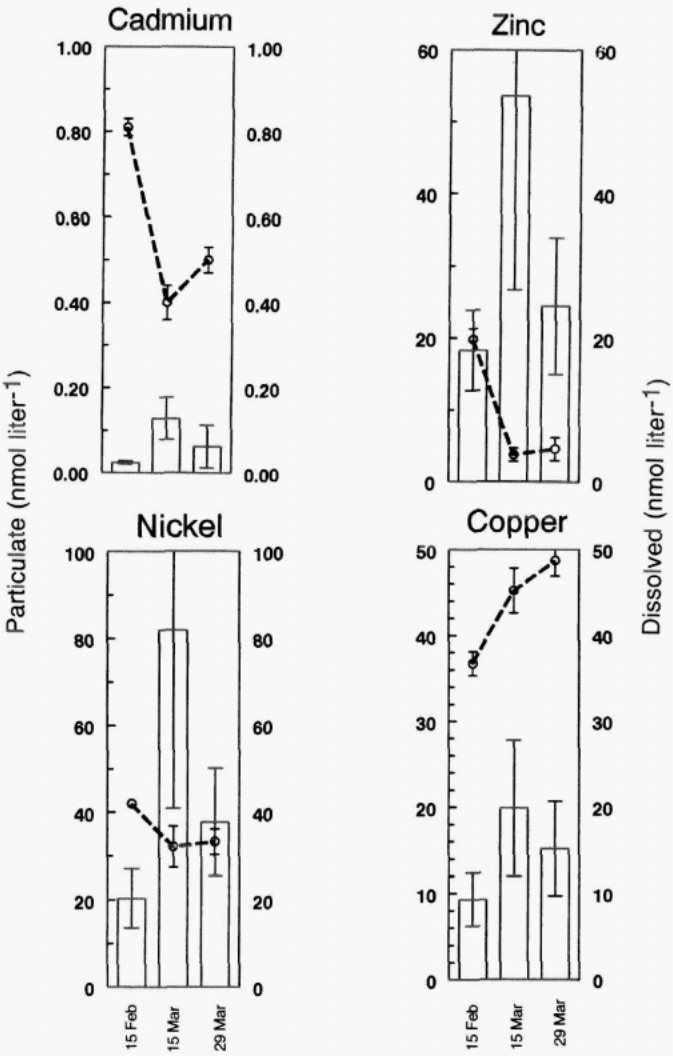

Fig. 4. Spatially averaged mass per unit volume of dissolved (line) and particulate (bar) cadmium, zinc, and copper in the waters of South San Francisco Bay on 15 February (before phytoplankton bloom), 15 March (midbloom), and 29 March (as the bloom receded).

Sinking and grazing of diatom-associated Cd most likely accounted for the difference. If indeed only 23% of total biogenic matter produced was in suspension on 15 March, then

$$(0.11 \text{ nmol liter}^{-1})/0.23 = 0.48 \text{ nmol liter}^{-1} \quad (3)$$

of particulate Cd was produced by the bloom; comparable to the 0.40 nmol liter^{-1} removed from the dissolved phase. It is difficult to directly estimate if sediment resuspension affected particulate or dissolved Cd because biological changes appeared to fully explain the changes in suspended particulate Cd.

Concentrations of Cd per unit mass of SPM increased during the bloom from 2.42 ± 0.59 nmol g^{-1} on 15 February to 4.87 nmol g^{-1} on 15 March (Table 4). If 20% of the change in mass of the SPM was phytoplankton-derived, and if all the increase in Cd concentration was phytoplankton uptake, then

Table 4. Mean concentrations of metals per unit mass suspended material and SD (in parentheses) compared to concentrations estimated in phytoplankton cells alone at a six-site transect in South San Francisco Bay on three dates in 1994: before the phytoplankton bloom (15 February), midbloom (15 March), and as the bloom receded (29 March). Estimates for phytoplankton Ni and Zn were derived from water-column depletion of metal and P; estimation of phytoplankton Cd was derived from changes in particulate concentration and proportion of suspended material attributable to the bloom (agrees with estimate derived from water column depletion) (nd; not determined).

	Cadmium	Copper	Nickel	Zinc
	(nmol g^{-1})		(μmol g^{-1})	
15 Feb	2.4(0.6)	0.9(0.1)	1.9(0.2)	1.7(0.2)
15 Mar	4.9(0.7)	0.7(0.1)	1.9(0.3)	1.9(0.3)
29 Mar	3.1(0.6)	0.8(0.1)	1.9(0.3)	1.2(0.2)
Phytoplankton alone	12.5	nd	0.04	0.68

$$(4.87 \text{ nmol g}^{-1} - 2.42 \text{ nmol g}^{-1})/0.2 = 12.5 \text{ nmol g}^{-1} \quad (4)$$

was the concentration in the algal cells themselves. This is greater than the 2.4 nmol Cd g^{-1} determined in prebloom SPM but at the lower end of the range of Cd concentrations calculated for plankton from the North Pacific (Bruland et al. 1994; Knauer and Martin 1973) (similar to the conclusion drawn from the Cd:P ratio derived from the dissolved depletion data). It is surprising for this urbanized estuary, but algal Cd concentrations do not appear to be substantially enriched in South Bay compared to nearby coastal waters. Both South Bay and the coastal Pacific are naturally Cd enriched by upwelling (van Geen and Luoma 1993; van Geen and Husby 1996).

In contrast to Cd, the increase in particulate Cu that coincided with the bloom appeared to be primarily influenced by resuspension (Fig. 4). One line of supporting evidence is the relationship observed between Cu and leachable Al in the particulate matter across all stations and sampling occasions (Fig. 5), indicating that changes in Cu concentrations were probably primarily a result of changes in particle size within the SPM (Klinkhammer and Bender 1981; Windom et al. 1989). The relationships of Cd, Ni, and Zn with leachable Al were not statistically significant when all data were considered (Fig. 5). If any Cu removal from solution by phytoplankton did occur, it was masked by Cu input to the water column from resuspension or, possibly, increased concentrations caused by production of organic ligands during the bloom (Ahner et al. 1995).

Increases in the mass of particulate Ni and Zn in the water column on 15 March were significantly larger than the corresponding reductions in dissolved metal concentrations (Fig. 4). Increased resuspended sediment would add substantial Zn or Ni to the water column because concentrations of these elements in sediments are high in San Francisco Bay (1.7–1.9 μmol Zn g^{-1}, 1.3 μmol Ni g^{-1}; Hornberger et al. in press), similar to concentrations in SPM (Table 4). At these sediment concentrations, the 20 mg liter^{-1} increase in SPM on 15 March would move 38 nmol Zn liter^{-1} and 27 nmol Ni liter^{-1} into the water column, similar to the actual changes that occurred. Thus, resuspension confounded de-

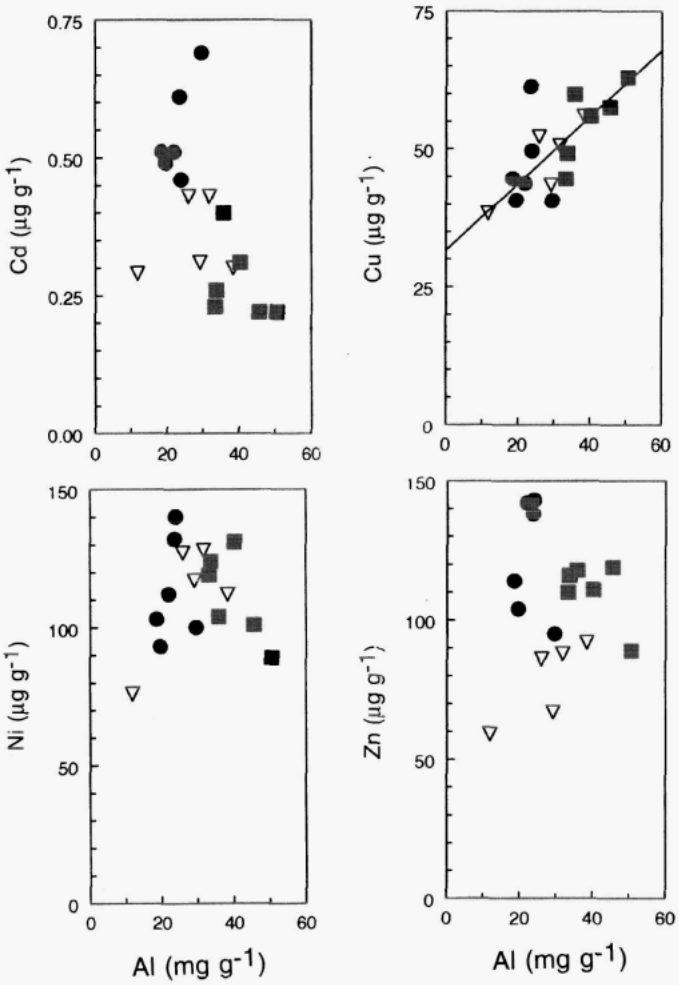

Fig. 5. Correlation of the concentration of cadmium, copper, nickel, and zinc with the concentration of leachable Al at three dates in South San Francisco Bay: before the phytoplankton bloom on 15 February (■), midbloom 15 March (●), and at the end of the bloom on 29 March (▽). Regression for Cu for all dates is $y = 33 + 15x$ ($r^2 = 0.49$, $P < 0.005$). Correlation of Zn, Cd, and Ni with Al was insignificant.

termination of algal uptake of Zn and Ni from particulate concentrations. From the stoichiometric ratios in Table 2, it is possible to estimate concentrations of Zn and Ni in phytoplankton themselves of 0.69 μmol Zn g^{-1} and 0.04 μmol Ni g^{-1} (Table 4).

Intracellular uptake may explain why Cd, Ni, and Zn were so strongly depleted from solution during the South Bay bloom. Phytoplankton uptake may include adsorption of metals to the new surface area provided by a bloom and(or) may involve active metal incorporation into cells. Large proportions of Cd and Zn, compared to many metals, are taken up into a labile intracellular fraction of phytoplankton (the cytosol), analogous to some nutrients (Collier and Edmonds 1984; Reinfelder and Fisher 1991). Intracellular uptake would add a new sink for these metals during a phytoplankton bloom, enhancing depletion from solution (*see* also Slauenwhite and Wangersky 1991; Reynolds and Hamilton-Taylor 1992; Rico et al. 1993). Intracellular uptake also has implications for recycling of these metals (Lee and Fisher 1992, 1993).

If the mass of Cd, Ni, and Zn passing through the phytoplankton in other estuaries is as large as that in South San Francisco Bay, then blooms are events that greatly amplify transformation of such elements in estuaries. Estuaries are considered traps for metals. Where anthropogenic nutrient inputs change blooms, our data indicate the trapping of trace elements may change concordantly. If conditions that increase bloom frequency or intensity could make metal trapping more efficient, then eutrophication and the effects of metal pollutants may be linked in ways not fully appreciated.

The complexity of estuarine processes can make it difficult to isolate biological influences on metal cycling. Nevertheless, we have shown in this work that the magnitude of biological effects on metals such as Cd and Zn can be impressive, whereas other metals (e.g. Cu) may be unaffected. Events like phytoplankton blooms can affect both dissolved and particulate concentrations of metals, such as Cd, that are accumulated into plant cytosol. The effects of blooms on metal concentration or mass associated with suspended particulate concentrations are particularly difficult to separate from resuspension if the metals occur in high concentrations in sediments. Although the effects of blooms can be substantial, their influences are most visible during small windows of opportunity (Murray 1987), and if the ecosystem is sufficiently understood to predict when critical events occur (as was the case in South Bay). Studies of the fate and effects of trace elements in estuaries must consider biological processes and events that determine biogeochemical cycling. Similarly, sampling designs and schedules of contaminant monitoring programs are incomplete unless they also consider the effects of phytoplankton.

Samuel N. Luoma

U.S. Geological Survey, MS465
345 Middlefield Rd.
Menlo Park, California 94025

Alexander van Geen

Lamont-Doherty Earth Observatory
Columbia University
Palisades, New York 10964

Byeong-Gweon Lee

USGS, MS465

James E. Cloern

USGS, MS496

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