Trace Metals (Cd, Cu, Ni, and Zn) and Nutrients in Coastal Waters Adjacent to San Francisco Bay, California

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ABSTRACT: Samples collected in December 1990 and July 1991 show that dissolved Cd, Cu, Ni, and Zn distributions in the Gulf of the Farallones are dominated by mixing of two end-members: (1) metal-enriched San Francisco Bay water and (2) offshore California Current water. The range of dissolved metal concentrations observed is 0.2–0.9 nmol kg^{-1} for Cd, 1–20 nmol kg^{-1} for Cu, 4–16 nmol kg^{-1} for Ni, and 0.2–20 nmol kg^{-1} for Zn. Effective concentrations in fresh water discharged into San Francisco Bay during 1990–1991 (estimated by extrapolation to zero salinity) are 740–860 μmol kg^{-1} for silicate, 21–44 μmol kg^{-1} for phosphate, 10–15 nmol kg^{-1} for Cd, 210–450 nmol kg^{-1} for Cu, 210–270 nmol kg^{-1} for Ni, and 190–390 nmol kg^{-1} for Zn. Comparison with effective trace metal and nutrient concentrations for freshwater discharge reported by Flegal et al. (1991) shows that input of these constituents to the northern reaches of San Francisco Bay accounts for only a fraction of the input to Gulf of the Farallones from the estuary system as a whole. The nutrient and trace metal composition of shelf water outside a 30-km radius from the mouth of the estuary closely resembles that of California Current water further offshore. In contrast to coastal waters elsewhere, there is little evidence of Cd, Cu, Ni, and Zn input by sediment diagenesis in continental shelf waters of California.

Introduction

Gordon (1980) showed that San Francisco Bay water is enriched in the dissolved trace metals Cd, Cu, Ni, and Zn relative to adjacent coastal water. Further sampling within the bay by Flegal et al. (1991) confirmed that San Francisco Bay water is enriched in these constituents relative to river water entering at the northern reaches of the estuary and saline water at the mouth (the Golden Gate), indicating significant inputs within the estuary. Flegal et al. (1991) also demonstrated that excess Cd, Cu, Ni, and Zn fluxes through the northern reaches of the estuary could be accounted for by local wastewater discharges. Even though highest dissolved metal concentrations were observed in the southern reaches of San Francisco Bay, corresponding flux estimates were not presented by Flegal et al. (1991). In addition, the true coastal water end-member contributing to the estuary could not be sampled at the Golden Gate since the tidal prism extends well into the Gulf of the Farallones (Peterson et al. 1989). We present here nutrient and trace metal data for nearshore samples collected along the coast south of the Golden Gate and along a transect extending to the edge of the continental shelf at the Farallon Islands. Our results constrain the composition of coastal water contributing to San Francisco Bay and indicate that shelf sediment

diagenesis does not appreciably enrich the overlying water column in Cd, Cu, Ni, and Zn off central California, in contrast to a number of other shelf regions. Extrapolation of our data to zero salinity also allows us to estimate the effective composition of fresh water discharged to the whole San Francisco Bay estuary during 1990–1991.

The origin of oceanic water masses mixing in the Gulf of the Farallones is determined by two principal features of circulation in the region: the direction of the current parallel to the coast, and the intensity of cross-shelf transport due to wind-driven coastal upwelling. The core of the California Current, about 200 km offshore from San Francisco Bay, flows south throughout the year and supplies relatively fresh subarctic water to the region (Hickey 1979). Over the continental shelf, the alongshore current component flows in the opposite direction, except when strong northwesterly winds are prevalent during spring and summer (Strub et al. 1987). The northwesterly winds induce a southerly flow over the shelf and also an offshore Ekman transport in the upper 20 m of the water column (Lentz 1987). A compensating onshore flow at depth was measured with current meters in the Gulf of the Farallones (Noble and Gelfenbaum 1990). The resultant coastal upwelling brings to the surface during spring and summer cold, saline, nutrient-rich Pacific water from as deep
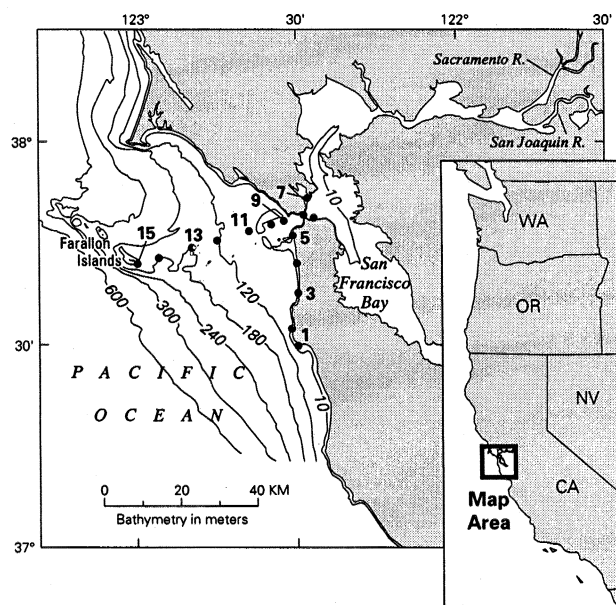
Fig. 1. Location of samples collected in December 1990 and July 1991. Bathymetry in meters.

TABLE 1. Results from replicate trace metal determinations in consistency standards. Uncertainty in recovery was calculated by propagating the standard deviation of the mean composition of spiked and unspiked coastal water. Detection limit calculated from variability of blank.

Ele-ment	Unspiked ± SD (nmol kg^{-1}) (n = 9)	Spiked ± SD (nmol kg^{-1}) (n = 11)	Recovery (%)	Blank (pg)	Detection Limit (nmol kg^{-1})
Cd	0.326 ± 0.035	0.641 ± 0.025	100 ± 6	0.006	0.003
Cu	3.0 ± 0.3	11.3 ± 0.6	96 ± 3	0.1	0.1
Ni	7.2 ± 0.6	20.0 ± 1.4	106 ± 5	0.2	0.2
Zn	2.4 ± 0.3	12.4 ± 1.2	80 ± 4	1.2	0.3

as 300 m under the California Current (Huyer 1983; van Geen et al. 1992).

Methods

Trace element samples were collected from the surf zone on December 19 and 21, 1990, and July 21, 1991. The samples were collected in acid-washed polyethylene bottles attached to a plexiglas holder at the end of a 3 m long wooden pole. Shore samples were collected in December 1990 between San Francisco Bay and Half-Moon Bay, 40 km to the south (Fig. 1). Salinity and nutrient samples were taken simultaneously from a separate bottle attached to the pole. Replicate trace element samples from the shore locations were taken at the same location within a few minutes. Surface water was also collected along a San Francisco Bay-Farallon Islands transect on July 20, 1991 (Fig. 1). Samples were taken with the same pole arrangement at ~1 knot from the side of a 12 m long power boat. All trace element samples were stored in the dark until filtration in the laboratory under a Class 100 laminar flow bench at the end of each sampling day. Trace element samples were filtered through an acid-washed 0.4 μm Nuclepore filter with an acid-washed Nalgene polycarbonate filtration system adapted for vacuum filtration and equipped with a Teflon O-ring. Nutrient samples were filtered through disposable 0.45 μm Durapore filters and acidified with 60 μl of 12 N Ultrex II HCl (Baker) per 60 ml of seawater. Dissolved silicate and phosphate were measured by spectrophotometry with a QuickChem AE flow-injection system (Lachat Instruments). Salinity was measured on samples stored in glass using an Autosal salinometer standardized with IAPSO water.

Low trace element water (Zn < 0.1 nmol kg^{-1}) used throughout the procedure was obtained from a combined Milli-RO/Milli-Q Plus system (Millipore Corporation). Trace element samples were acidified with 0.5 ml 12 N Ultrex II HCl per 250 ml of seawater. Cd, Cu, Ni, and Zn contributions from this acid were not detectable. Trace elements were preconcentrated from 18 ml to 1 ml by metal-ligand adsorption onto a resin column using an improved version of the automated device described by van Geen and Boyle (1990). The procedure was modified by using sub-boil distilled NH$_4$OH (40–120 μl per 18 ml sample) to raise the pH to about 8.5. The strength of HNO$_3$ in the distilled ethanol eluent was reduced to 0.05 N, and sample eluates were evaporated to dryness at room temperature in a laminar flow bench. Consistency of results between each batch of ten samples was determined by including a composite coastal seawater sample in the procedure, as well as a spiked aliquot of this sample with a factor of 2- to 5-fold higher Cd, Cu, Ni, and Zn concentrations (Table 1).

Sample eluates were taken up in 1 ml of 0.03 N nitric acid (Ultrex II) and 0.025 N phosphoric acid for determination by graphite furnace atomic absorption spectroscopy (GFAAS) with a Perkin-Elmer Zeeman 3030 instrument. Phosphoric acid was cleaned by passing through a small Dowex AG 50W-X8 cation-exchange resin. Table 1 lists the reproducibilities of trace metal determinations for the spiked and unspiked consistency standards and the calculated mean recovery factor used to calculate final metal concentrations in the samples. Cd, Cu, Ni, and Zn blanks for the procedure were determined by preconcentrating a 1 to 10 dilution of surface water from the Sargasso Sea with Milli-Q (MQ) water. Surface water from this region contains very little Cd and Zn, and relatively low Cu and Ni concentrations: 0.002 nmol kg^{-1}, 0.06 nmol kg^{-1}, 2.3 nmol kg^{-1}, and 1.2 nmol kg^{-1}, respec-

TABLE 2. Nearshore samples collected in December 1990 and July 1991. * indicates likely contamination. Sample replicates a and b were collected within a few minutes of each other. Nutrients in μmol kg^{-1}. Trace metals in nmol kg^{-1}.

Sta-tion	Location	Date	Salinity	Si	P	Cd	Cu	Ni	Zn
1a*	Pillar Point	December 19, 1990	33.427	22.4	0.47	0.323	4.4	16.3	11.1
1b*						0.312	2.5	11.8	3.2
1		July 21, 1991	33.541	3.1	0.78	0.330	1.8	4.5	0.6
2a	Moss Beach	December 19, 1990	33.333	1.7	0.39	0.193	1.1	4.8	0.9
2b						0.204	1.5	6.7	1.8
2		July 21, 1991	33.540	5.8	0.83	0.372	2.1	5.6	1.4
3a	San Pedro	December 19, 1990	32.529	23.2	0.76	0.446	8.8	10.3	3.4
3b						0.431	9.0	9.1	3.1
4a	Edgemar	December 19, 1990	32.288	31.5	2.10	0.517	10.6	12.2	5.4
4b						0.555	9.6	11.8	4.2
5	Point Lobos	December 21, 1990	32.648	26.5	0.54	0.509	6.5	10.3	6.8
6	Crissy Field	December 21, 1990	31.946	36.3	1.24	0.594	9.2	14.4	10.8

TABLE 3. Richardson Bay–Farallon Island transect, July 20, 1991. * indicates likely contamination. Nutrients in μmol kg^{-1}. Trace metals in nmol kg^{-1}.

Station	Location	Water Depth	Salinity	Si	P	Cd	Cu	Ni	Zn
7	Richardson Bay	3	32.185	35.9	2.35	0.897	20.7	14.9	20.1
8	Golden Gate	56	32.509	30.5	1.93	0.744	13.4	11.7	8.5
9	Point Bonita	24	32.581	28.6	1.83	0.748	12.2	14.1	8.2
10	Gulf of the Farallones	16	32.726	25.8	1.65	0.669	12.4	12.3	7.4
11	Gulf of the Farallones	28	32.426	≤1.0	≤0.1	0.209	3.8	4.9	0.4
12*	Gulf of the Farallones	43	33.213	9.1	0.37	0.539	41.8	9.0	3.0
13	Gulf of the Farallones	55	33.479	4.8	0.51	0.353	3.4	5.3	0.5
14	Gulf of the Farallones	55	33.260	10.0	0.78	0.292	1.4	4.4	1.0
15	Farallon Island	40	33.168	6.8	0.37	0.244	1.3	5.4	0.2

tively (Bruland and Franks 1983). Uncertainties in blank corrections are small relative to the range of trace metal concentrations in this data set. The matrix used to calibrate the GFAAS instrument was also preconcentrated 1:10 Sargasso Sea water/ MQ water. Apparent Ni recoveries greater than 100% indicate this matrix does not exactly match that obtained by preconcentrating full-strength seawater (Table 1). Corrections listed in Table 1 which combine matrix effects and recovery efficiencies for all four metals were applied to all data in Tables 2 and 3.

Results

Dissolved Cd, Cu, Ni, and Zn concentrations in the replicate samples from stations 2, 3, and 4 collected from the surf zone were virtually identical (Fig. 1; replicates are labelled a and b in Table 2). This indicates that despite resuspension of sand by waves, and variable amounts of sediment trapped in replicate sample bottles, a representative value for the composition of surf zone water can be obtained from shore-based sampling. There are exceptions such as the significantly elevated dissolved Cu, Ni, and Zn concentrations in sample 1a relative to 1b collected at Pillar Point. Sampling artifacts in this variable environment can be minimized by

taking replicates. Since dissolved silicate concentrations at Pillar Point were also elevated relative to Moss Beach (22 vs 1.7 μmol kg^{-1}), samples 1a and 1b may not be representative and are not discussed further. The composition of San Francisco Bay water sampled from Crissy Field in December 1990 (sample from station 6) was within the range of nutrient and trace metal concentrations observed by Gordon (1980) and, more recently, by Flegal et al. (1991).

The composition of coastal waters in the Gulf of the Farallones shows the influence of upwelling. Concentrations of silicate, phosphate, Cd, Cu, Ni, and Zn in the region at salinities >33‰ are similar to concentrations in deep water from the California Current (Bruland 1980; Fig. 2). Dissolved silicate, phosphate, and Cd concentrations in the more nearshore waters of the Gulf of the Farallones increase linearly with decreasing salinity, suggesting conservative mixing between San Francisco Bay water and coastal water (Fig. 2a). The relations are more scattered for Cu, Ni, and Zn (Fig. 2b) than for nutrients and Cd. Samples collected shipboard from the Gulf of the Farallones in July 1990 also suggest a mixing relationship, albeit between a San Francisco Bay end-member containing about twice as much phosphate, Cd, Cu, and Zn relative to
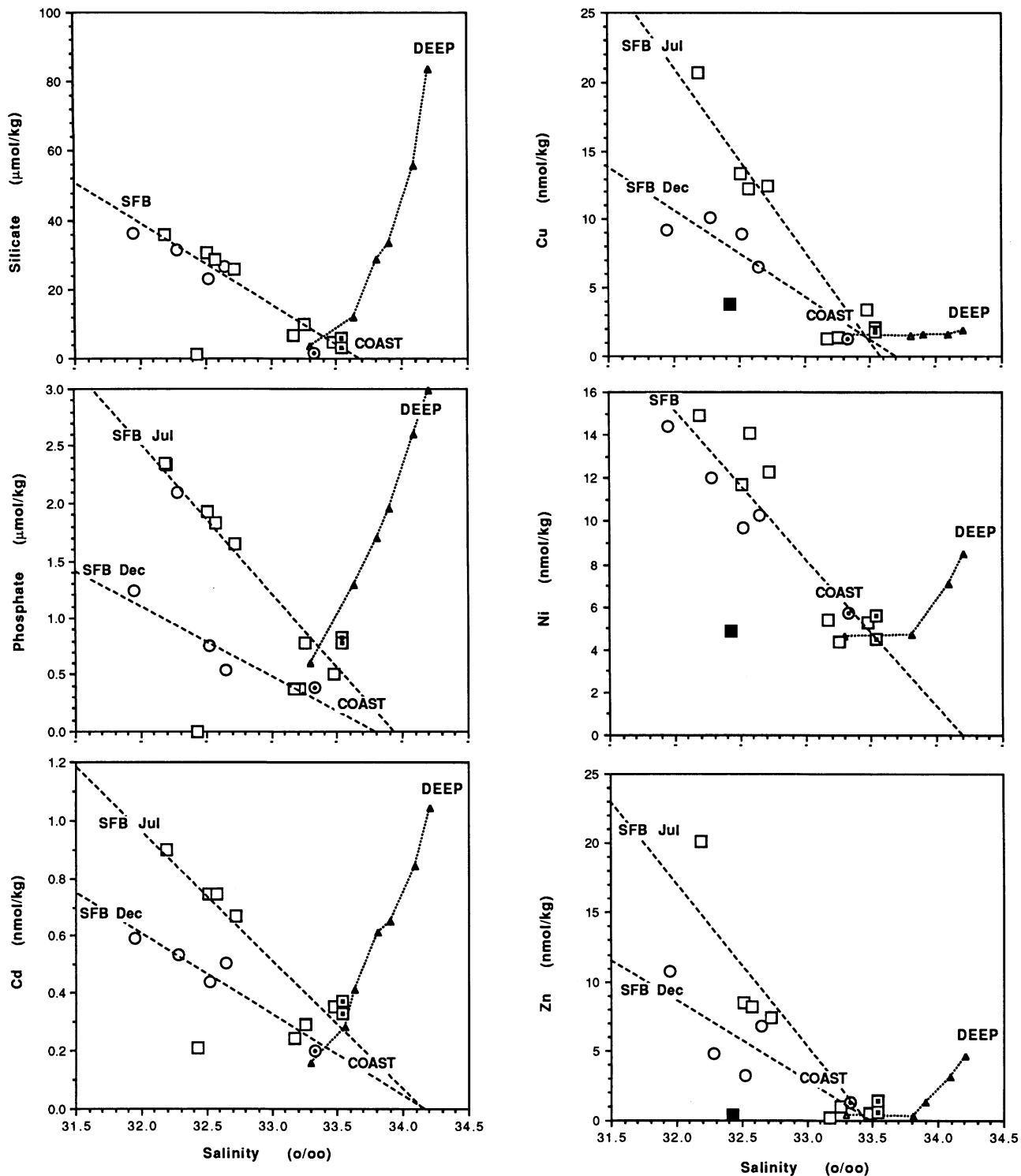
Fig. 2. Left) Dissolved silicate, phosphate, and Cd as a function of salinity for nearshore and transect samples, and for a profile of California Current water at 36°52′N, 122°53′W collected by Bruland (1980). Right) Same as in (left) for dissolved Cu, Ni, and Zn. Circles: nearshore samples, December 1990. Squares: samples from Farallon transect and Pillar Point/Moss Beach, July 1991. Circles and squares filled at center indicate Moss Beach/Pillar Point samples collected in December 1990 and July 1991. Dotted line connecting small triangles indicates composition of upper 500 m of water column in the California Current. Samples collected at nearshore station (1) and transect station (12) discussed in text are not included. Black square shows composition of sample from station (11). SFB (Dec, Jul): San Francisco Bay end-member (December and July); COASTAL: surface coastal water; DEEP: California Current water at 500 m depth. Regression lines between surface coastal water and San Francisco Bay water extrapolate to the effective freshwater discharge concentrations discussed in text. Linear regressions do not include samples collected at stations 1, 11, and 12 for all tracers. Station 4 was excluded for the phosphate regression.

seven months earlier and coastal water enriched in phosphate and Cd due to active upwelling (van Geen et al. 1992). Comparison of the work of Gordon (1980), Flegal et al. (1991), and our own data suggests that there is a recurrent seasonal pattern of higher dissolved phosphate, Cd, Cu, and Zn concentrations during summer in San Francisco Bay. Kuwabara et al. (1989) also observed a seasonal change in dissolved Cd concentrations at their station closest to the central bay (station 27). Note that all dissolved Cd concentrations reported in Kuwabara et al. (1989) should be halved to correct for an error in data reduction (J. S. Kuwabara written communication).

Samples from two stations listed in Table 3 do not fit the simple linear relationships. For sample (11), midway between the Golden Gate and San Francisco Bay, nutrient concentrations were at the detection limit of 1 μmol kg^{-1} and 0.1 μmol kg^{-1} for silicate and phosphate, respectively. Cd, Ni, and Zn concentrations were also somewhat lower than observed at the sample furthest offshore (sample 15) despite a 0.7‰ lower salinity at sample (11). This suggests that an isolated patch of offshore water from the north may have been entrained by the meandering California Current. The second outlier is the sample from station 12, which contained extremely elevated Cu levels (Table 3). This sample was probably contaminated at the time of collection (e.g., by trapping of a Cu-rich flake of antifouling paint).

Discussion

Phosphate and Cd are enriched in California Current surface water (0.6 μmol kg^{-1} and 0.16 nmol kg^{-1}, respectively) relative to surface water of the North Pacific central gyre (0.06 μmol kg^{-1}, and 0.002 nmol kg^{-1}). Bruland (1980) attributed this pattern to upwelling of Pacific water that is strongly enriched in phosphate and Cd. Concentrations of dissolved phosphate and Cd in surface water at Pillar Point, Moss Beach (0.8 μmol kg^{-1}, and 0.35 nmol kg^{-1}, respectively), and the outer stations of the Gulf of the Farallones are higher than in the California Current but are consistent with the composition of upwelled water at this salinity. Satellite-derived surface temperature data for the region confirm that upwelling is stronger nearshore (Schwing et al. 1991). The higher salinity and concentrations of phosphate and Cd at Pillar Point and Moss Beach in December 1990 than in July 1991 are consistent with the seasonal cycle in coastal upwelling (Huyer 1983). For the intervening period of maximum upwelling (May–June 1991), van Geen et al. (1992) reported phosphate and Cd concentrations at Pillar Point (2.8 μmol

kg^{-1} and 0.8 nmol kg^{-1}, respectively) higher than ever had been measured in surface waters of the California Current (Martin et al. 1976; Bruland 1980; Bruland et al. 1985). Depletion of silicate and phosphate at Pillar Point and Moss Beach relative to the vertical mixing relationships suggests that nutrients may be taken up more rapidly in surface water than a trace element with a nutrient-type vertical distribution in the ocean such as Cd.

Whereas part of the seasonal increase in Cd concentrations within San Francisco Bay can be explained by the effect of upwelling on the composition of coastal water, this is not the case for Cu, Ni, and Zn. As noted by Flegal et al. (1991), potential enrichments due to upwelling of water from the upper few hundred meters of the California Current are limited for Cu, Ni, and Zn (Fig. 2). The work of Gordon (1980), Flegal et al. (1991), and our own data suggest a source of Cd, Cu, Ni, and Zn within San Francisco Bay that is, somehow, expressed more strongly during summer. Potential factors are sediment resuspension and mixing of pore waters into the water column during summer when winds are strongest in San Francisco Bay as well as a reduced influx of fresh water during the same period that increases the residence time of bay water.

Effective concentrations of fresh water discharged to the ocean from San Francisco Bay as a whole can be calculated by extrapolating the respective trace metal-salinity relations in the Gulf of the Farallones to zero salinity (Boyle et al. 1974). The linear regressions in Fig. 2 extrapolated to zero salinity would yield intercepts of 800 ($\pm$60) μmol kg^{-1} for silicate; 21 ($\pm$4) μmol kg^{-1} and 44 ($\pm$6) μmol kg^{-1} for phosphate in December and July, respectively; 10 ($\pm$2) nmol kg^{-1} and 15 ($\pm$2) nmol kg^{-1} for Cd in December and July, respectively; 210 ($\pm$50) nmol kg^{-1} and 450 ($\pm$50) nmol kg^{-1} for Cu in December and July, respectively; 240 ($\pm$30) nmol kg^{-1} for Ni; and 190 ($\pm$70) and 390 ($\pm$60) nmol kg^{-1} for Zn in December and July, respectively. Effective freshwater nutrient and metal concentrations calculated by Flegal et al. (1991) for the northern reaches of San Francisco Bay only are between 3 and 50 times smaller. Despite the considerable uncertainties in such estimates, this comparison suggests that inputs to central and/or south San Francisco Bay dominate the flux of nutrients and trace metals exported to the Gulf of the Farallones.

A simple calculation shows that nutrient input from San Francisco Bay to the Gulf of the Farallones is at least as high as the input due to upwelling Pacific subsurface water. During a 5-d period of strong upwelling off northern California, Lentz (1987) measured a rate of cross-shelf exchange of

2.3 m² s⁻¹ per unit length of coastline. This determination compares well with a mean onshore flow of 1.5 m² s⁻¹ per unit length of coastline between 20 m and 65 m depth estimated from current meters deployed in the Gulf of the Farallones between May and October 1989 (Noble and Gelfenbaum 1990). Assuming mean silicate and phosphate deep water concentrations of 25 μmol kg⁻¹ and 1.5 μmol kg⁻¹ for upwelling source waters, respectively, the rate of nutrient input integrated over the 30 km length of shelf strongly affected by the outflow from San Francisco Bay is 1,100 moles s⁻¹ and 70 moles s⁻¹ during spring and summer. Mean silicate and phosphate input for the year should be about a factor of two lower since the intensity of upwelling decreases by an order of magnitude during fall and winter (Huyer 1983). Both 1989 and 1991 were low rainfall years and freshwater input to the south bay is very small. Therefore, mean freshwater discharge to the north bay quoted by Flegal et al. (1991) of 2.9 × 10⁵ m³ s⁻¹ can be combined with effective freshwater end-member nutrient concentrations estimated above to calculate an input of silicate and phosphate to the Gulf of the Farallones from San Francisco Bay of 230 moles s⁻¹ and 9 moles s⁻¹. Within the uncertainties of these estimates, it appears that the flux of nutrients from San Francisco Bay to the Gulf of the Farallones is comparable to the nutrient input sustained by upwelling. This may contribute to particularly elevated phytoplankton pigment concentrations in the Gulf of the Farallones measured by the Coastal Zone Color Scanner between March and July 1981 (Abbott and Zion 1987).

Dissolved metal concentrations in nearshore waters at Pillar Point and Moss Beach, and shelf waters near the Farallon Islands are comparable to levels in the upper few hundred meters of the California Current (Fig. 2; Bruland 1980). Thus, shelf sediment diagenesis does not significantly enrich the overlying water column in the region. This contrasts with observations of metal enrichments in waters of the Bering Sea (Heggie 1982; Heggie et al. 1987), Atlantic coastal waters of North America (Bruland and Franks 1983), and European coastal waters (Kremling 1983; Kremling and Hydes 1988; Kremling and Pohl 1989). However, data for slope waters off the Washington coast from Jones and Murray (1984), a nearshore transect between Washington and California (van Geen in preparation), and Pacific coastal waters near the United States-Mexico border (Sañudo-Wilhelmy and Flegal 1991) confirm that there is no strong interaction between Pacific shelf sediments and the water column for Cd, Cu, Ni, and Zn along the western United States coast. Note that Johnson et al. (1992) recently showed that California shelf sediments are a significant source of Mn to shallow coastal waters.

River input of dissolved metals cannot explain differences in metal enrichments between western and eastern coastal waters since concentrations of Cd, Cu, Ni, and Zn in major rivers of the world rarely differ by more than a factor of two, and are much lower than the extrapolated metal-salinity relation for eastern shelf waters would predict (Bruland and Franks 1983; Shiller and Boyle 1991). It also seems unlikely that the amount or composition of sediment deposited could explain this difference. Sediment discharge by western rivers (70 × 10⁶ t yr⁻¹) is four times higher than for eastern rivers because the sediment yield normalized to watershed area is seven times higher in the west (Milliman and Meade 1983).

Upwelling and the resulting rapid exchange of shelf water with the open ocean may be one reason that shelf sediment diagenesis has no significant imprint on dissolved Cd, Cu, Ni, and Zn concentrations in United States Pacific coastal waters. Despite comparable freshwater input per unit length of coastline for the west and east coasts (UNESCO 1979), there is a 2‰ larger difference in salinity between continental shelf waters and slope waters in the east than in the west (Csanady and Hamilton 1988). This in itself indicates that cross-shelf exchange may be more pronounced off the west coast. Csanady and Hamilton (1988) estimate from salt balance that the rate of exchange of slope and shelf waters in the Mid-Atlantic Bight is on the order of 0.2 m² s⁻¹ per unit length of coastline. Because upwelling is seasonal and weaker off Oregon and Washington than off California (Huyer 1983), a representative estimate for the west coast as a whole may be on the order of 0.6 m² s⁻¹ rather than the rate of 2.3 m² s⁻¹ measured locally over a short period by Lentz (1987). A second difference between the west and east coasts of the United States is the average width of the continental shelf to the 200 m isobath. The former is on the order of 25 km wide and the latter 200 km. Corresponding to these shelf geometries and cross-shelf exchange rates, mean residence times of continental shelf water would be 2 mo for the west coast and 3 yr for the east coast. Note, however, that particularly pronounced dissolved metal enrichments off Spain and Portugal, where the shelf is relatively narrow and seasonal upwelling strong, suggest that the rate of cross-shelf exchange may not be a determining factor everywhere (van Geen et al. 1990; van Geen et al. 1991).

Conclusions

Distributions of salinity, silicate, phosphate, and dissolved Cd, Cu, Ni, and Zn in the Gulf of the

Farallones can to a large extent be explained by conservative mixing of water from central San Francisco Bay with coastal water. Effective freshwater nutrient and trace metal concentrations extrapolated from the data suggest that inputs to central and/or south San Francisco Bay are the main source of these constituents to the Gulf of the Farallones. Outside the region dominated by mixing with San Francisco Bay water, the composition of shelf water is comparable to water of the California Current 100 km offshore. Distributions of salinity, nutrients, and Cd in surface waters of the Gulf of the Farallones indicate that upwelling originates from greater depth under the California Current toward the coast. December 1990 and July 1991 distributions of these tracers are consistent with the seasonal cycle in the strength of northwesterly winds that drive coastal upwelling. A lack of significant trace metal enrichments due to shelf sediment diagenesis in western United States coastal waters is probably due to the narrow continental shelf and rapid cross-shelf circulation.

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