CROATICA CHEMICA ACTA CCACAA **70** (1) 389–417 (1997)

ISSN-0011-1643
CCA-2429

Original Scientific Paper

Porewater Gradients and Diffusive Benthic Fluxes of Co, Ni, Cu, Zn, and Cd in San Francisco Bay*

Ignacio Rivera-Duarte and A. Russell Flegal

Earth Science, WIGS, Earth and Marine Sciences Building,
University of California, Santa Cruz, CA 95064

Received February 6, 1996; accepted August 21, 1996

In order to determine the remobilization of Co, Ni, Cu, Zn, and Cd from the sediments, gradients of their dissolved (< 0.45 μm) and particulate concentrations were measured in both relatively pristine and contaminated sediments of San Francisco Bay, as well as relatively pristine adjacent embayments (Tomales Bay and Drakes Estero). Three mechanisms were determined to regulate the diagenetic release of those elements to porewaters: (i) the degradation of organic matter in oxic and suboxic zones; (ii) the reduction of Mn in suboxic zones; and (iii) the formation of soluble metal-sulfide complexes in anoxic zones. While the estimated diffusive benthic fluxes of Ni, Cu, and Cd were relatively small (≤ 10%) compared to their riverine fluxes, the estimated diffusive benthic fluxes of Co and Zn were similar (≈ 100%) to their riverine inputs. These initial estimates also indicate that the total (dissolved and particulate) benthic remobilization of Co, Ni, Cu, and Zn is greater than either riverine or point source inputs of those elements to San Francisco Bay. Moreover, those benthic inputs are projected to become more significant as the anthropogenic inputs of those elements, from both point sources and non-point sources, are reduced.

INTRODUCTION

San Francisco Bay (Figure 1) is a severely impacted urban estuary, with inputs of contaminants from numerous natural and anthropogenic sources.[1] The accumulative impact of these multiple inputs is evidenced by non-con-

---

* Dedicated to Marko Branica on the occasion of his 65th birthday.

servative excesses of some trace element (Ag, Cd, Co, Cr, Cu, Mn, Pb, Zn) concentrations in the northern reach of the estuary, which are tentatively attributed, in part, to remobilization from sediments.[2–5] The impact is more pronounced in surface waters of South Bay, where anomalously high levels of some trace elements (Cu, Ni, Pb) approach or exceed current environmental health standards.[6] Those excesses appear to be due to a combination of direct anthropogenic inputs (point source discharges, surface runoff, and atmospheric deposition) and natural processes that release trace elements from contaminated sediments.[3,4,7–9]

The relative importance of benthic fluxes of trace elements appears to have been elevated by decreases in fluxes from other sources. These decreases include the 90% reduction in some trace element loading in point sources during the past three decades, which has resulted from efforts to improve the water quality in San Francisco Bay.[10] Since elemental concentrations in surface waters of the Bay have remained relatively unchanged during the last ten years despite those efforts,[1] it appears that benthic remobilization from contaminated sediments has become increasingly responsible for the persistence of trace metal contamination in San Francisco Bay.[1,3,4,7,8]

The relative importance of benthic fluxes of some trace elements (Cu, Cd and Pb) in San Francisco Bay has been shown in previous studies. One preliminary study indicates that diffusive benthic fluxes of Pb (3 to 31 mol d^{-1}) from sediments on the periphery of the Bay are at least one order of magnitude above the fluvial input (0.2 mol d^{-1}) of dissolved Pb to the estuary.[8] The study also indicates that the estimated net benthic flux of dissolved Pb (6 to 186 mol d^{-1}) is within an order of magnitude of the anthropogenic input

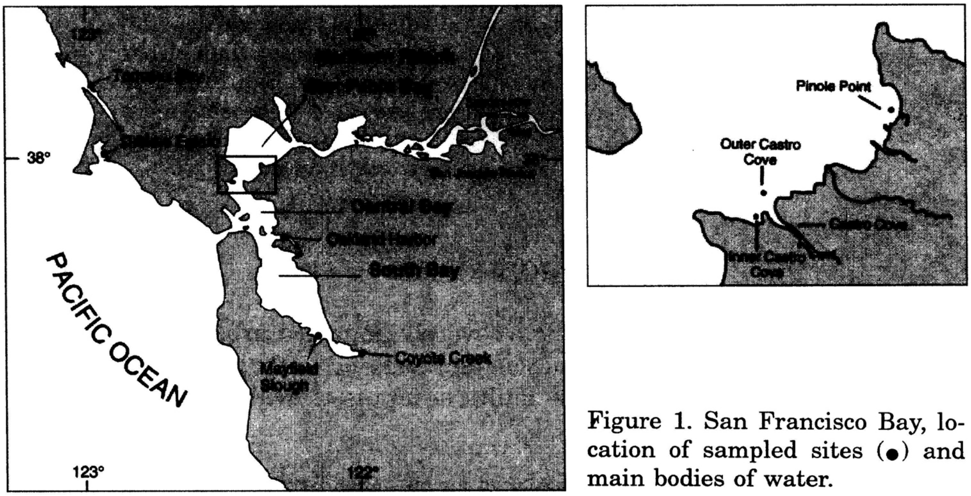

Figure 1. San Francisco Bay, location of sampled sites (●) and main bodies of water.

of total (dissolved and particulate) Pb (965 to 8,410 mol d^{-1}) to the estuary.[8] Another study indicates that the net benthic flux of Cu (–2,817 to 483 mol d^{-1}) can be similar to its anthropogenic input from point sources (441 to 724 mol d^{-1}) and the net benthic flux of Cd (–145 to 250 mol d^{-1}) can be one order of magnitude greater than its anthropogenic input from point sources (36 mol d^{-1}) to the estuary.[11]

Consequently, the present study was designed to provide a more systematic estimate of the release of trace elements from the sediments in San Francisco Bay. It includes the following analyses of Co, Ni, Cu, Zn, and Cd concentrations in porewaters and sediments from both relatively pristine and contaminated sediments in different regions of the estuary. The analyses indicate two important pathways for the remobilization of trace elements from the sediments: (i) diffusion and advection of trace elements released at the sediment-water interface and (ii) advection (*i.e.*, irrigation by macrofauna) of elements released in deeper porewaters. For example, diffusive and advective benthic fluxes are both estimated to be comparable to the riverine inputs of dissolved Co and Zn, while the inputs from benthic fluxes are much smaller for Ni (≈ 10%), Cd (≈ 2%), and Cu (≈ 1%). Those estimates are corroborated by complementary steady-state mass-balance calculations and estimations of resuspension loads, which indicate that benthic remobilization, sediment resuspension, and phase transformations of elements with suspended particles are now the principal processes regulating total (dissolved and particulate) elemental concentrations in surface waters of the estuary.

Study Area

Statistical analyses of elemental and nutrient concentrations and ancillary data in surface water indicate four different biogeochemical regions within San Francisco Bay estuary.[3] These are (i) the low-salinity area in the northern reach directly influenced by the Sacramento and San Joaquin Rivers, (ii) a transition area centered in San Pablo Bay with intermediate salinity ($S = 12$ to 23), (iii) the Central Bay area with high salinities ($S = 27$ to 32); and (iv) the South Bay, a seasonal lagoon with high salinities ($S = 27$ to 31) and anomalously high elemental concentrations during periods with limited hydraulic flushing (Figure 1). Within these regions, nine sites are studied for trace elements in porewaters and sediments, as well as for the respective nutrient distributions.[12] Most of the sites located within San Francisco Bay are relatively contaminated (*i.e.*, Coyote Creek, Mayfield Slough, Oakland Harbor, Castro Cove, Inner Castro Cove, and Outer Castro Cove), while one site (*i.e.*, Pinole Point) is relatively pristine. Since these sites have the characteristic of being either relatively contaminated or relatively pristine they are considered representative of extreme conditions within San Francisco

Bay. Additional samples are collected from other relatively pristine sites in two adjacent embayments (*i.e.*, Tomales Bay and Drakes Estero). In addition to degrees of contamination, there is variance between locations with respect to sediment characteristics such as tidal and hydraulic dispersion, presence of macroorganisms, percent of particulate organic matter, sediment grain size, presence of anoxic zones, thickness of oxic and suboxic zones, and Mn and Fe reduction zones (Table I). While analyses of these disparate sites provided a more systematic perspective on variations in elemental cycles within the estuary, the numerous differences among the sites made between- site comparisons difficult.

EXPERIMENTAL

Trace metal clean techniques were used in sampling and analyses. These were conducted in class-100 trace metal clean work stations.[8,12] Cores (10 cm diameter, 40 cm length) were collected directly from the sediment at each of the sampling sites. A whole core squeezer,[13] modified for trace element collection, was used in the extraction of porewater from the nepheloid layer and from ten depths in the sediment (1, 2, 4, 6, 8, 10, 14, 18, 22, and 26 cm). The porewater samples were immediately filtered (0.45 µm acid-cleaned Teflon filters). The initial 5 to 10 mL of porewater were used to condition the sampling equipment for trace element sampling, and for the determination of ancillary (e.g., nutrients) parameters.[12] The final 1 to 10 mL were aliquoted into acid-cleaned polyethylene bottles, acidified ($pH < 2$) with sub-boiling quartz distilled (2×) 6 N HCl, double bagged, and stored for at least one month before proceeding with the elemental preconcentration. Samples of sediment were obtained from the corresponding depths for porewater, and stored in acid-cleaned polyethylene containers until analyzed.

The elements in the acidified porewater aliquots were concentrated using an ammonium 1-pyrrolidine dithiocarbamate (APDC) and diethylammonium diethyldithiocarbamate (DDDC) liquid-liquid extraction,[14] which was modified to a microtechnique for use with small samples.[15] Elemental concentrations were determined in the preconcentrated aliquots with a Perkin-Elmer Model HGA 500 graphite furnace and a Perkin-Elmer Model 5500 atomic absorption spectrometer (GFAAS) with continuous background correction, using stabilized platforms and the method of standard additions. Average concentrations determined in concurrent analyses of nearshore seawater reference material CASS-2 (Canadian National Research Council) were not significantly different at $p < 0.05$ (t-test) from their certified values for Co, Ni, and Cu, and at $p < 0.01$ for Zn, and Cd. Average method blanks (≈ 50 mL, $pH < 2$, 18 MΩ cm^{-1} water) ranged from 0.02 to 0.05 nM for Co, from 0.08 to 0.05 nM for Ni, from 0.07 to 0.02 nM for Cu, from 0.29 to 0.11 nM for Zn, and from 1.4 to 0.53 pM for Cd. Limits of detection, calculated as three times the standard deviation of the method blanks, were 0.18 nM for Co, 0.22 nM for Ni, 0.24 nM for Cu, 1.1 nM for Zn, and 34 pM for Cd. Preconcentration ranges in recovery and extraction efficiencies, as determined by analysis of an internal porewater reference material, were from 96 to 100% and 90 to 104%, respectively.[15]

TABLE I.

General characteristics of the sediment porewater sites sampled in San Francisco Bay, Tomales Bay, and Drakes Estero. A more detailed description of those sites is given in Rivera-Duarte and Flegal.[12]

	Coyote Creek	Mayfield Slough	Oakland Harbor	Castro Cove	Inner Castro Cove	Outer Castro Cove	Pinole Point	Tomales Bay	Drakes Estero
Location in Bay	South Bay	South Bay	South/ Central Bay	San Pablo Bay	San Pablo Bay	San Pablo Bay	San Pablo Bay	Out of Bay	Out of Bay
Contaminated	Waste water	Waste water	Maritime	Oil	Oil	Oil	No	No	No
Location w.r.t. tides	Inter tidal	Inter tidal	Sub tidal	Inter tidal	Inter tidal	Sub tidal	Sub tidal	Inter tidal	Inter tidal
Macrobiota	No	No	Yes	Yes	Yes	Yes	Yes	Yes	Yes
% TOC range	1.3–3.4	1.7–2.4	1.0–3.0	1.3–2.3	1.9–3.2	0.8–1.4	0.1–1.1	0.1–0.3	0.1–0.6
% Clay & silt	90	95	87	99	97	90	78	4	7
Oxic / Suboxic (cm)	0	0	< 1	0	< 1	< 1	< 1	> 26	> 22
Mn red.	Strong	Strong	Strong	Weak	Weak	Strong	Strong	No	No
Fe red.	Strong	Strong	Strong	Weak	Strong	Strong	Strong	No	No
Suboxic / Anoxic (cm)	6	22	> 26	8	4	> 22	> 22	–	–

w.r.t. = With respect to.
red. = Reduction zone.

Near-total particulate concentrations were determined after aqua- regia digestion.[16] These are defined as »near-total« concentrations because the refractory alumino-silicates were not totally dissolved with HF, and some refractory organics may not have been totally destroyed by ashing the sample prior to the analyses. GFAAS was used to measure near-total concentrations of Cd and Cu, and inductively coupled plasma-atomic emission spectroscopy (ICP-AES) was used for the determination of near-total concentrations of Co, Ni, and Zn. The percent recoveries (≥ 68 %) of the particulate analyses as determined by concurrent analyses of reference sediments (BCSS-1, MESS-1, PACS-1, and MESS-2 from the National Research Council Canada) are listed in Table II. Procedural blanks were ≤ 2% of the particulate elemental concentration in those standard reference materials and in samples.

TABLE II.

Recoveries (%) for the determination of near-total particulate concentrations of Cd, Co, Cu, Ni and Zn in sediment reference materials BCSS-1, MESS-1, PACS-1, and MESS-2 from the National Research Council Canada.

	Cd	Co	Cu	Ni	Zn
BCSS-1	97	87	68	90	81
MESS-1	99	94	71	92	82
PACS-1	87	104	83	108	97
MESS-2	91	82	85	81	75

RESULTS AND DISCUSSION

Comparisons with Porewater Elemental Concentrations in Other Systems

There is good agreement between measured dissolved elemental (Co, Ni, Cu, Zn, and Cd) porewater concentrations in San Francisco Bay and previously reported concentrations in other porewater. These include analyses of sediment porewaters in estuarine, hemipelagic, and pelagic environments. This relative consistency is illustrated in Table III, which lists the ranges in dissolved elemental concentrations from several different systems, with their within-site variations in different redox zones as defined by Rivera-Duarte and Flegal.[12] In brief, this criteria requires the presence of minimal dissolved Fe and Mn in the oxic zone, and peak concentrations of dissolved Fe, Mn, HPO_4^{2-}, and NH_4^+ within the suboxic zone. For the anoxic zone the criteria includes negligible Fe and Mn concentrations, decreasing concentrations of SO_4^{2-} and HPO_4^{2-}, coupled to evidence of the presence of S^{2-}.

Comparisons Between Surface Water and Porewater Elemental Concentrations within the Estuary

There are also similarities between the elemental concentrations in surficial sediment porewaters and surface waters within San Francisco Bay.

TABLE III.

Comparison of porewater concentrations in different coastal and estuarine environments. The redox zonation was inferred from the criteria of Rivera-Duarte and Flegal in the cases where it was not defined by the author(s).[12] Some of the concentrations were obtained from plots, not from tables. Therefore, the magnitude of the values, rather than the actual concentrations, were compared in the text.

Location	Redox	Co (nM)	Ni (nM)	Cu (nM)	Zn (nM)	Cd (nM)
Narragansett Bay	Suboxic		0–150	20–400		
(Elderfield, 1981)	Anoxic		< 10	10–50		
Long Island Sound	Suboxic			80–420		2
(Lyons & Fitzgerald, 1983)	Anoxic			< 30		3–4
Pelagic & hemipelagic	Oxic		8–92	15–100		
sediments	Suboxic		10–800	50–200		
(Sawlan & Murray, 1983)	Anoxic		10–40	1–40		
Puget Sound	Suboxic		35–130	35–183		20–90
(Emerson *et al.*, 1984)	Anoxic		10–60	20–60		0–10
Gullmarsfjorden (Westerlund *et al.*, 1986)	Anoxic		9.5–17	1.6–2.4	5–12	0.02–0.1
Gullmarsfjorden (Sundby *et al.*, 1986)	Anoxic	0.3–2				
Laurentian Trough	Oxic					0.20–5.2
(Gobeil *et al.*, 1986)	Suboxic					0.05–1.9
Southern California Borderland	Oxic	0–5	0–40	0–70		
(Shaw *et al.*, 1990)	Suboxic	5–60	25–600	0–120		
Point Sur California (McCorkle & Klinkham-mer 1991)	Suboxic					0.1–2.5
Tyrrhenian Sea (Ciceri *et al.*, 1992)	Suboxic	3–119	30–170	8–48	250–2500	1–9
San Francisco Bay	Oxic	3.8–60	16–356	8.4–70	29–1019	0.048–1.3
	Suboxic	0.2–115	0.3–439	0.5–140	4–2603	0.001–4.2
	Anoxic	0.3–74	5.5–259	3.2–158	12–614	0.026–2.4
Tomales Bay and Drakes Estero	Oxic	0.3–10	1.2–134	0.3–299	3–185	0.003–1.9

The ranges and average concentrations of some dissolved elements (Co, Ni, Cu, Zn, Cd) in surface waters of the sediment core sites in San Francisco Bay are shown with the corresponding porewater concentration gradients in Figures 2 to 6. These dissolved concentrations in surface waters were measured during twelve different cruises between April 1989 and February 1995, and include low riverine flow (caused by a protracted drought from 1986 to 1992), average, and high riverine flow periods (Ref. 3, unpublished data). The comparison was done with surface water concentrations because there are no comparable data on most elemental concentrations in bottom waters

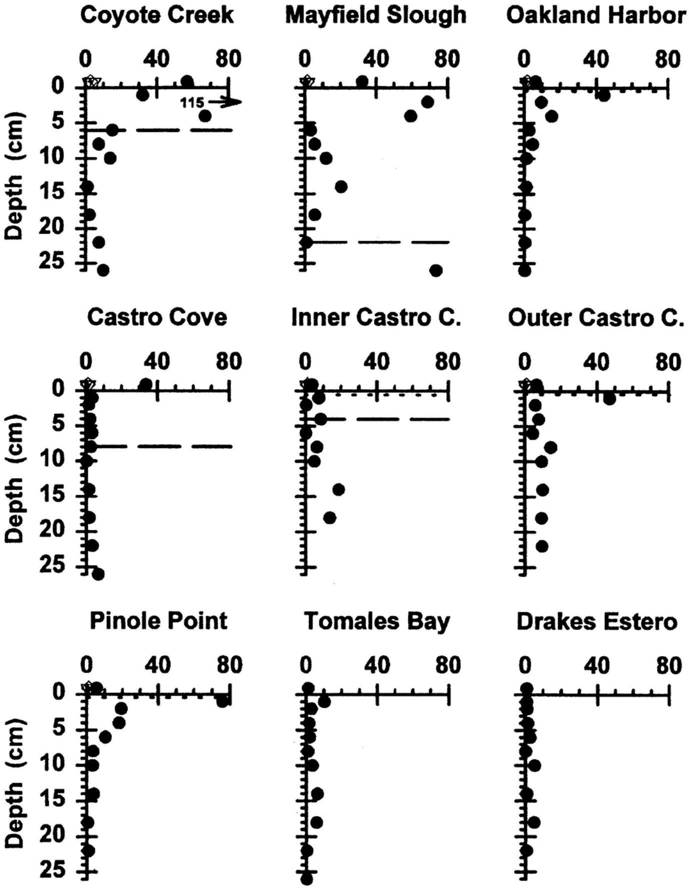

Figure 2. Porewater concentration (nM) gradients of dissolved (< 0.45 µm) Co (●). The concentration above 0 cm deep corresponds to the nepheloid layer. The range (∇) and average (⊕) concentration in surface water are shown for the purposes in text. The oxic/suboxic (•••) and the suboxic/anoxic (– – –) fronts are those defined by Rivera-Duarte and Flegal.[12]

in San Francisco Bay, which is relatively shallow (mean depth ≈ 5 m)[17] and well mixed, and there are no measurable vertical changes in the concentrations of Cu and Cd in deeper regions of the estuary.[11]

These comparisons indicate that concentrations of dissolved Ni, Cu, and Cd are in the same order of magnitude in surface waters and surficial oxic/suboxic sediment porewaters (*e.g.*, nepheloid layer and 1 cm depth). In contrast, Co and Zn concentrations were as much as one or two orders of magnitude higher in the porewater than their ranges in surface water. This is consistent with similar comparisons reported for coastal suboxic sedi-

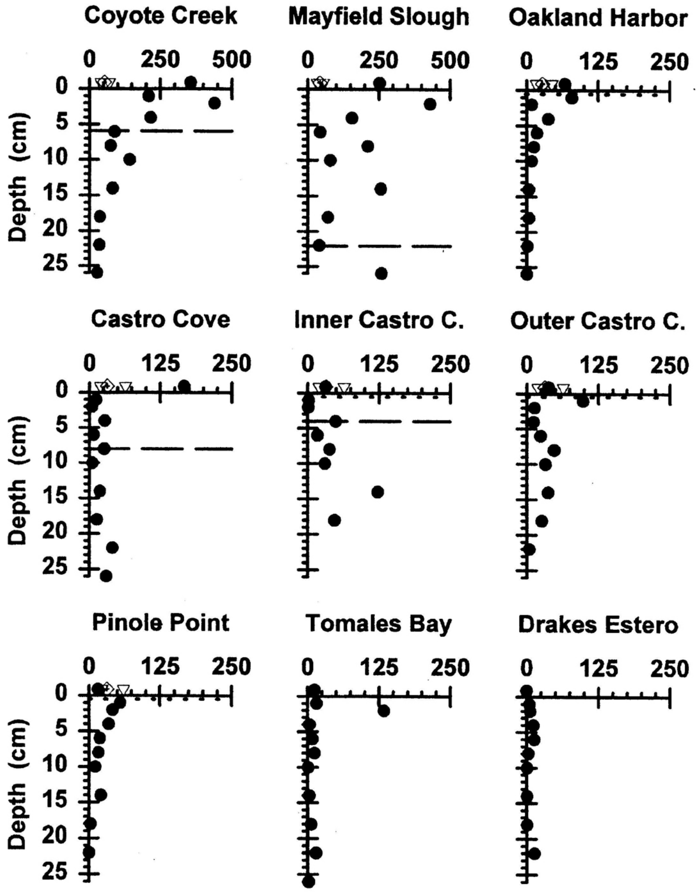

Figure 3. Porewater concentration (nM) gradients of dissolved (< 0.45 μm) Ni (●). The concentration above 0 cm deep corresponds to the nepheloid layer. The concentration range is to 500 nM at Coyote Creek and Mayfield Slough, and it is to 250 nM at the other sites. The range (∇) and average (⊕) concentration in surface water are shown for the purposes in text. The oxic/suboxic (•••) and the suboxic/anoxic (– – –) fronts are those defined by Rivera-Duarte and Flegal.[12]

ments, where concentration factors between porewater and overlying seawater were: < 1 for Cu, 1–10 for Cd and Ni, 10–100 for Co, and 1–100 for Zn.[18]

In principle, the relative similarity of the concentration ranges in surface waters and porewaters of dissolved Cu, Ni, and Cd suggest both limited interchanges between sediments and overlying waters and temporal variations in the direction of their diffusive benthic fluxes. The latter is substantiated by a recent report that seasonal net benthic fluxes of Cu and Cd are correlated

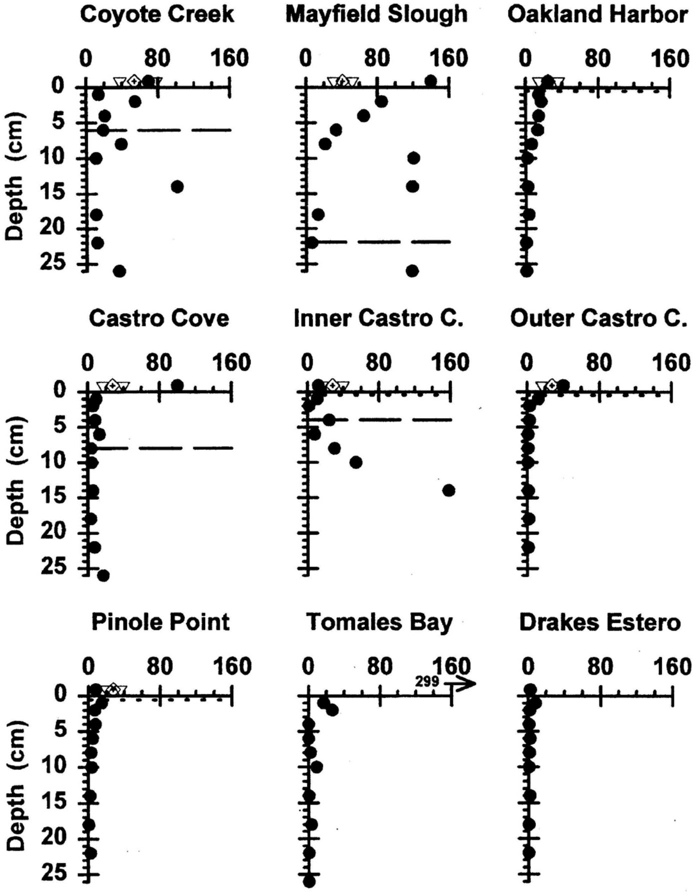

Figure 4. Porewater concentration (nM) gradients of dissolved (< 0.45 μm) Cu (●). The concentration above 0 cm deep corresponds to the nepheloid layer. The range (∇) and average (⊕) concentration in surface water are shown for the purposes in text. The oxic/suboxic (•••) and the suboxic/anoxic (– – –) fronts are those defined by Rivera-Duarte and Flegal.[12] The nepheloid layer concentration (299 nM) in Tomales Bay was above the range in concentration.

with variations in the direction of DOC fluxes in the South Bay.[11] It is also corroborated by a report that the net benthic fluxes of Cu, Zn and Cd correspond to the oxidation of carrier phases in the surficial (≤ 1 mm) layer of coastal sediments.[19] Therefore, variations in the inputs and oxidation of carrier phases appear to regulate the release of Cu, Ni, Zn and Cd to porewaters and their subsequent remobilization in San Francisco Bay and other coastal regimes.

The presence of carrier phases can also affect the benthic remobilization of Co. Excess concentrations in surficial sediment porewater of Co and Zn,

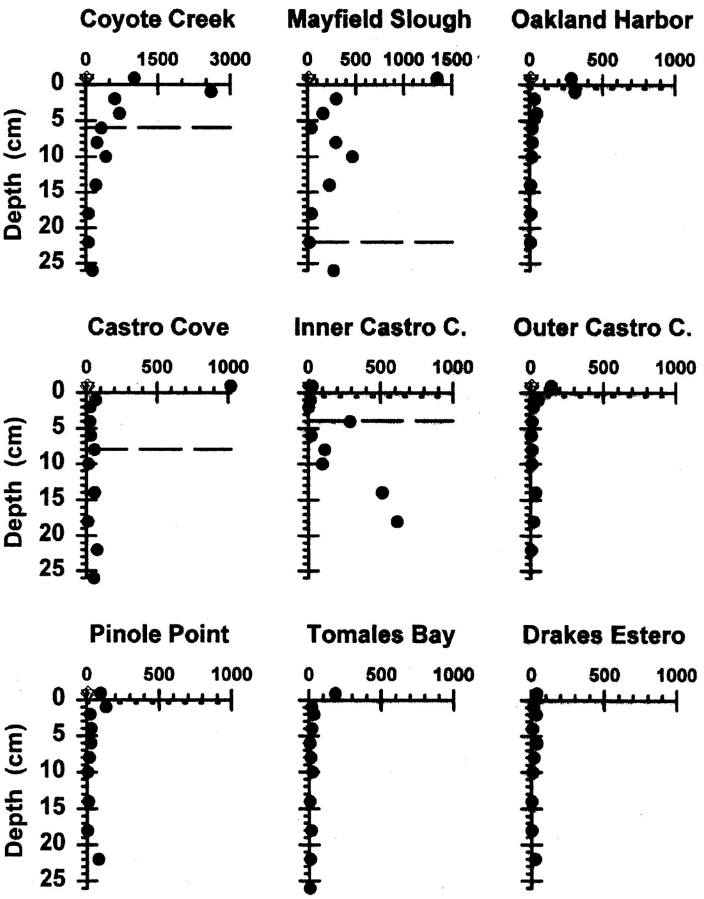

Figure 5. Porewater gradient concentration (nM) of dissolved (< 0.45 μm) Zn (●). The concentration above 0 cm deep corresponds to the nepheloid layer. The range in concentration for Coyote Creek is from 0 to 3,000 nM, while the range for the rest of the stations is less than 1,500 nM. The range (∇) and average (⊕) concentration in surface water are shown for the purposes in text. The oxic/suboxic (•••) and the suboxic/anoxic (- - -) fronts are those defined by Rivera-Duarte and Flegal.[12]

relative to surface waters, suggest their continuous diffusive remobilization in San Francisco Bay. However, the association of Co (and HPO_4^{2-}) with particulate Fe and Mn oxyhydroxides was suspected in the measurement of negative (*i.e.*, to the sediment) net benthic fluxes of Co in anoxic sediments covered by oxic waters elsewhere.[20] Other factors which influence elemental fluxes at the sediment-water interface are discussed in the next section.

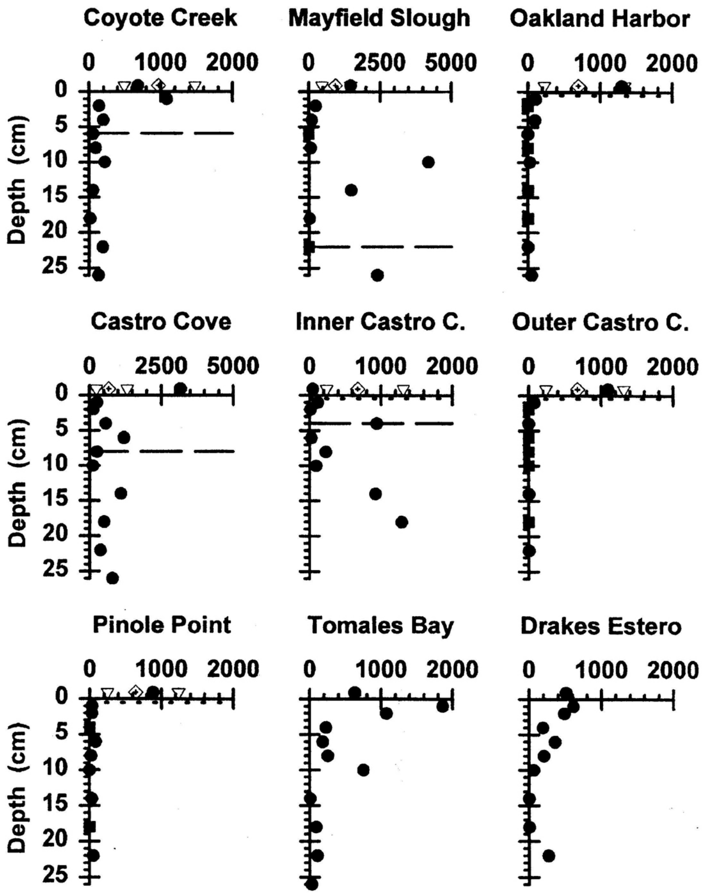

Figure 6. Porewater concentration (pM) gradients of dissolved (< 0.45 μm) Cd (●). The concentration above 0 cm deep corresponds to the nepheloid layer. Concentrations below the limit of detection ($3s_{BLANKS}$) are depicted as ■. Mayfield Slough and Castro Cove have a concentration range of 0 to 5,000 pM, while the rest of the stations have a range of less than 2,000 pM. The range (∇) and average (⊕) concentration in surface water are shown for the purposes in text. The oxic/suboxic (•••) and the suboxic/anoxic (– – –) fronts are those defined by Rivera-Duarte and Flegal.[12]

Effect of Redox Sequence on the Release of Trace Elements to Porewaters

All of the surficial sediments sampled in the San Francisco Bay sites were suboxic. This was evidenced by their redox sequence, using porewater gradient profiles of dissolved (< 0.45 μm) nutrients (*e.g.*, NH_4^+, H_4SiO_4, SO_4^{2-}, HPO_4^{2-}), dissolved and particulate Fe and Mn, and dissolved and total organic carbon (Table I). This suboxic condition is attributed to the layer (4 to > 22 cm thick) of fine (< 62.5 µm) sediments and organic detritus that cover the bottom of the Bay. Some contaminated stations (*i.e.,* Inner Castro Cove) revealed anoxic conditions below the suboxic zone. In contrast, sediments in adjacent relatively pristine embayments (Tomales Bay and Drakes Estero) are sandy (> 62.5 µm) and oxic to ≈ 30 cm, with particulate near-total concentrations at least one order of magnitude lower than those in San Francisco Bay sites (Figure 7).

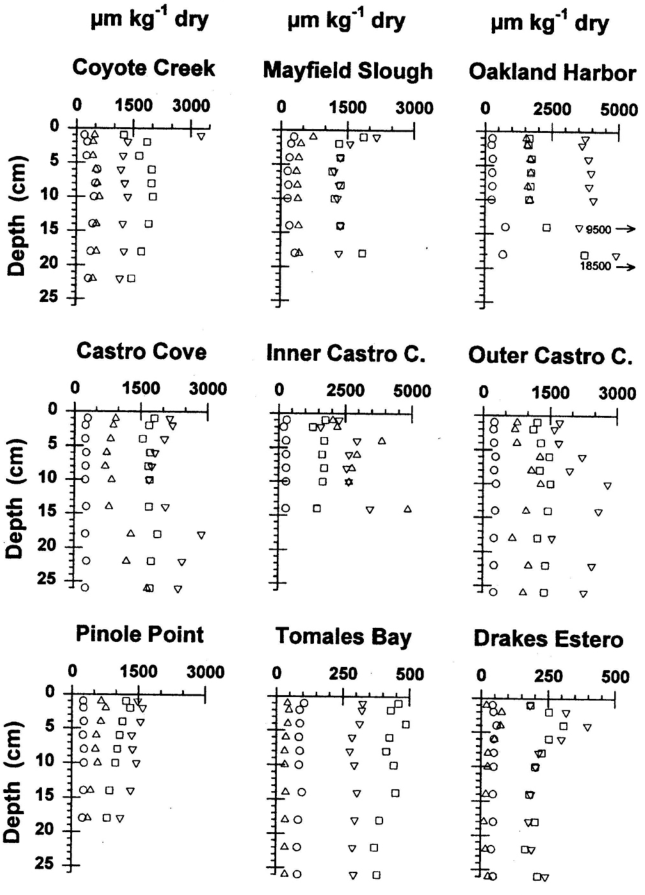

Figure 7. Particulate concentrations (µm kg^{-1} dry sediment) gradients of Co (O), Ni (□), Cu (Δ), and Zn (∇). Note the different concentration ranges (500, 3000, and 5000 µm kg^{-1} dry sediment). Two subsamples of Cu in Oakland Harbor, 14 (9,500 µm kg^{-1} dry sediment) and 18 (18,500 µm kg^{-1} dry sediment) cm deep are out of the plotted range. Cadmium was not plotted because it is two to three orders of magnitude lower in concentration than the other elemental concentrations.

The spatial variations in those redox conditions were used to characterize the diagenetic release of dissolved (< 0.45 μm) trace elements to porewaters. Figure 8 provides a schematic characterization of the elemental geochemistry in porewater concentration gradients. This characterization is similar to that in Shaw *et al.*,[21] but it includes an additional highly anoxic zone where several elements are mobilized. As illustrated in these stylized profiles, the release of trace elements into the porewaters of San Francisco Bay occurs in three zones: (i) the oxic or suboxic nepheloid layer, (ii) the zone of Mn reduction within suboxic conditions, and (iii) the zone of formation of soluble sulfide complexes in well developed anoxic conditions. The patterns for the release of trace elements in the nepheloid layer closely resembles their sorption sequence to humic acids.[22,23] The patterns are also consistent with theoretical predictions based on the Irving-Williams order (Figure 9), with dissolved A-type elements decreasing and B-type elements increasing in concentration within the anoxic zone.[24]

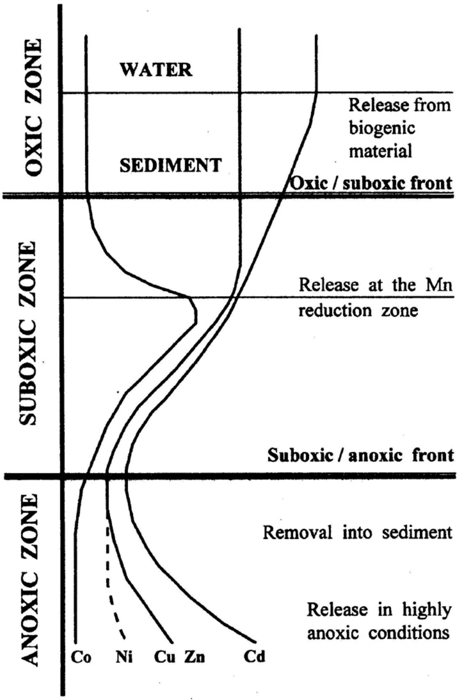

Figure 8. Schematic representation of the porewater concentration gradients observed in relatively pristine and contaminated sites within San Francisco Bay. This characterization is similar than those from Shaw *et al.*[21]

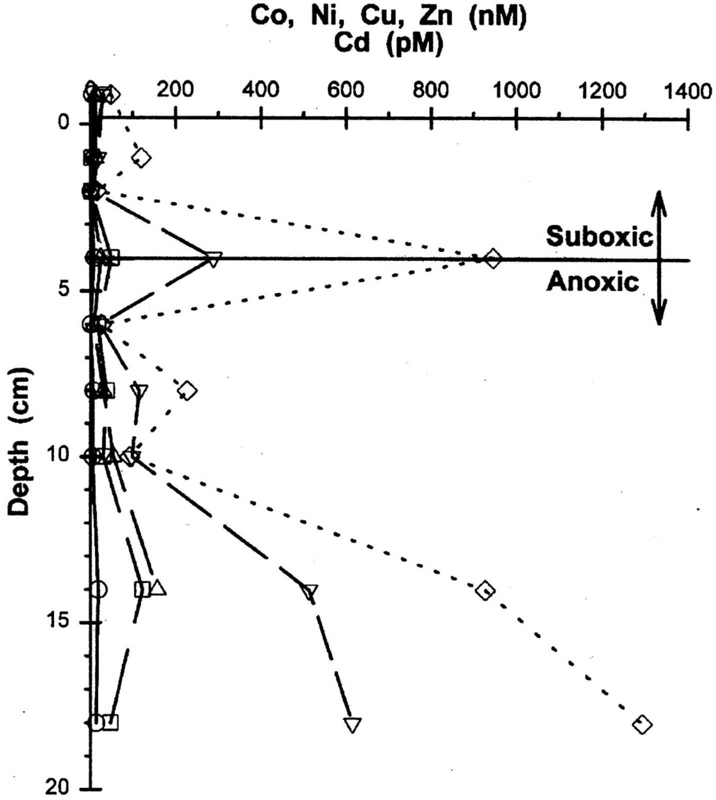

Figure 9. Porewater concentration gradients of trace elements in Inner Castro Cove. The top 4 cm of the sediment are suboxic, while anoxic conditions are well developed below there. The contrast between the relative constant concentration of dissolved Co (O) and the increase in the concentrations of dissolved Ni (□), Cu (Δ), Zn (∇), and Cd (◊) is correspondent with the Irving-Williams order.

Processes Affecting the Remobilization of Dissolved Trace Elements out of the Sediments

Once the elements are released to porewaters they are affected by processes that may induce their remobilization to overlying waters from different sediment depths. Diffusion and advection are both important for fluxes of elements released at or near the sediment- water interface, but only advection is important for fluxes of elements released in deep porewaters (Figure 10). Consequently, the three main mechanisms for the release of trace elements act at different depths and the rates and depths of elemental remobilization are variable.

Early diagenesis of easily degradable organic matter appeared to account for peak concentrations of Ni, Cu, Zn, and Cd at the sediment-water interface (Figures 3–6). The association of these trace elements with natural organic matter has been shown to be important in model systems,[25] other natural waters,[26] other interstitial waters,[27,28] and surface waters of San Francisco Bay.[11,29,30,31] These elements have more B-type character than Co, which did not exhibit a concentration peak at that interface (Figures 2, 8). This contrast is consistent with the sorption of trace elements (Cu > Cd > > Zn > Ni > Co) to humic acid in an acidic aqueous solution (pH 5.8) and sediments.[22,23] In theory, those elements are released from easily degradable organic matter at the sediment-water interface and diffuse into overlying waters (Figure 10), where they are reabsorbed onto organic material or inorganic particles, and redeposited to the sediments.[32]

Peak concentrations of dissolved Co, Ni, Cu, and Zn (Figures 2 to 5, 8) were also present at sites with strong Mn reduction (Coyote Creek, Mayfield Slough, Oakland Harbor, Outer Castro Cove, and Pinole Point), but not at sites with weak Mn reduction and strong Fe reduction (Castro Cove and Inner Castro Cove). This is consistent with reports of the release of Co, Ni and Cu in the Mn reduction zone in anoxic waters[33,34] and in coastal,[35] hemipelagic, and pelagic sediments.[21,36] It is also consistent with the reported remobilization of Co from sediments, which has been inversely linked to the adsorption capacity of metal oxides (most probably Mn) in the absence of easily degradable organic matter.[20]

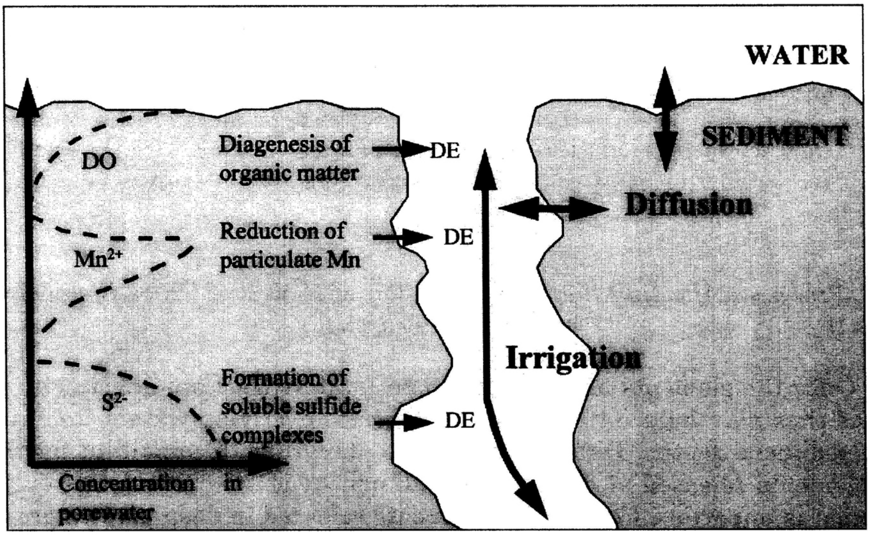

Figure 10. Schematic representation of the processes affecting the remobilization of dissolved elements from porewaters in sediments of San Francisco Bay.

There were increases in the concentrations of dissolved Ni, Cu, Zn, and Cd in well-developed anoxic zones (Figures 3 to 6, 8, 9). These increases are attributed to the formation of soluble sulfide complexes and metallo-organic-sulfur derivatives of humic and fulvic acids. All of these metal cations are either B-type or cations with more B-type character in the Irving-Williams order,[37] and they are prone to form soluble complexes with S^{2-} and HS^-.[24,38,39,40] Therefore, under conditions of continuous increase in dissolved sulfide species (*i.e.*, anoxic conditions) dissolved B-type elements will increase in concentration,[24] as was observed in San Francisco Bay.

In contrast, there was no increase of dissolved Co in those anoxic zones. This element has more A-type character,[37] and does not form soluble sulfide complexes. Again, this observation agrees with theoretical predictions.

There is evidence of the continuous benthic flow of dissolved sulfide during the annual cycle[11] and of the presence of submicromolar concentrations (< 1 nM to 162 nM) of sulfides in San Francisco Bay waters.[41] Consequently, there appears to be a remobilization of soluble metal-sulfide complexes, which are advected from deeper anoxic sediments by bioturbation, irrigation, and physical mixing processes. Previous analyses have shown that this advection can extend to a depth of 50 cm in the South Bay.[42]

In summary, porewater concentration gradients indicate three principal pathways for the release of dissolved chemical species from sediments within San Francisco Bay. These include the release from easily degradable organic matter at the sediment-water interface, the release from manganese oxyhydroxides in the suboxic zone, and the release of soluble metal-sulfide complexes in the anoxic zone (Figures 8 and 9). The subsequent transport of these dissolved species to overlying waters is caused by both diffusion and advection near the sediment-water interface, but it is only caused by advection in deeper sediments (Figure 10). The estimations presented in the following sections substantiate the proposal that these benthic fluxes are an important source of trace elements to waters of San Francisco Bay.[8] [11]

Diffusive Benthic Fluxes of Elements Released at or near the Sediment-Water Interface.

Average dissolved trace element concentrations in surface waters of San Francisco Bay were used to estimate magnitude and direction of the benthic diffusion of trace elements released at or near the sediment- water interface. The averages were calculated for stations located close to the sites sampled for porewater, and are shown with the respective porewater concentration gradients (Figures. 2 to 6). Diffusive benthic fluxes of trace elements were estimated from the gradient between those annual average surface water concentrations and peak surficial porewater concentrations by applying the first law of Fick:

$$F_j = -\phi D_s (dC_j / dx)$$

where F_j is the diffusive flux of the j ion or molecule into the sediments (mole cm_b^{-2} s^{-1}), ϕ is the porosity of the sediment, D_s is the sediment diffusion coefficient (cm_b^2 s^{-1}), and dC_j /dx is the change in concentration of the dissolved j species with depth in the sediment (mol cm_p^{-4}) (the subscript b indicates that concentrations and distances are measured over the bulk sediment, and the subscript p indicates the porewater phase only). Porosities were measured from the water content of the sediments. Estimates of D_s were derived from the empirical relation of Iversen and Jørgensen,[43] and corrected for average annual bottom water temperatures[44] by the Stokes-Einstein relation. The detailed procedure for these calculations is described in another report.[12]

Calculated sediment diffusion coefficients in the nepheloid layer ranged from 5.2 to 5.6×10^{-6} cm_b^2 s^{-1} for Co and Ni, 5.4 to 5.7×10^{-6} cm_b^2 s^{-1} for Cu, 5.5 to 6.0×10^{-6} cm_b^2 s^{-1} for Zn and Cd. The ranges of D_s in the top couple of centimeters in the sediment were from 3.0 to 3.7×10^{-6} cm_b^2 s^{-1} for Co and Ni, 3.1 to 3.8×10^{-6} cm_b^2 s^{-1} for Cu, 3.2 to 4.0×10^{-6} cm_b^2 s^{-1} for Zn and Cd. In general, D_s remained essentially constant (0.1×10^{-6} cm_b^2 s^{-1}) in the top couple of centimeters of each core. These D_s values agree with the specific sediment diffusion coefficients calculated by Hammond *et al.* for San Francisco Bay, which were 6.0 to 6.5×10^{-6} cm_b^2 s^{-1} in the summer, 5.0 to 5.5 × $\times 10^{-6}$ cm_b^2 s^{-1} in the fall, and 3×10^{-6} cm_b^2 s^{-1} in the winter.[42] The ranges in calculated D_s are also in good agreement with the effective sediment diffusion coefficient (10.7×10^{-6} cm_b^2 s^{-1}) in Gullmarsfjorden, Sweden,[45] and the D_s for Cd (1.9×10^{-6} cm_b^2 s^{-1}) in the Laurentian Trough.[40] The San Francisco Bay values are also similar to the D_s values for Ni^{2+} (3.16×10^{-6} cm_b^2 s^{-1}), Cu^{2+} (4.03×10^{-6} cm_b^2 s^{-1}), and Zn^{2+} (4.04×10^{-6} cm_b^2 s^{-1}) in sediments of Clearwater Lake, Ontario.[46]

Irrigation of Sediments, Benthic Fluxes of Trace Elements Released in Deeper Sediments

Elements released in deeper sediments may be remobilized by irrigation.[12,42,47–50] Since the effect of irrigation could not be determined from our measurements, the three zone irrigation model proposed by Hammond *et al.* was used to estimate the fluxes due to the irrigation of the sediment.[42] In this model:

$$F_j = -\phi D_S (dC_j / dx) + \sum {}^i h_i \lambda'_i (C_w - C_i)$$

h_i is the thickness of zone i (cm_b), λ'_i is the irrigation rate constant (s^{-1}), C_w the average concentration in the overlying water column as described before, and C_i is the average concentration in porewaters throughout zone i (mol cm$_b^{-3}$). The λ'_i estimated by Hammond *et al.* for a shoal station during summer ($\lambda'_i = 2 \times 10^{-6}$ s^{-1}; $\lambda'_2 = 0.52 \times 10^{-6}$ s^{-1}) were used in the calculations.[42] The thickness of both zones were estimated from the porewater concentration gradients of H_4SiO_4 and NH_4^+, as described by Rivera-Duarte and Flegal.[12] The three zone irrigation model was not applied in the sediment cores of both Coyote Creek and Mayfield Slough, because there were no macroorganisms in sediment cores at those sites. The fluxes due to irrigation were added to those by diffusion from the nepheloid layer in order to approximate net benthic fluxes.

The results for the estimated diffusive fluxes and the fluxes due to irrigation of the sediments are listed in Table IV, along with measured and estimated fluxes from other benthic systems. The estimated diffusive fluxes for Ni and Zn were one order of magnitude larger in sites affected by waste water discharges (*i.e.*, Coyote Creek and Mayfield Slough). Still, the estimated diffusive and net (irrigation plus diffusive) benthic fluxes, were generally within the same range of both the net benthic fluxes of Cu and Cd in the center of the South Bay.[11] They were also comparable to diffusive and net benthic fluxes reported for other suboxic coastal sediments.[18]

These calculations indicate that benthic fluxes of dissolved Co were systematically out of the sediment. Both estimated diffusive and irrigation-based benthic fluxes of Co were always positive (*i.e.*, out of the sediment), which agrees with reports of Co fluxes in other suboxic sediments.[18] In contrast, minimal net benthic fluxes of Co were measured in anoxic sediments (*i.e.*, absence of Mn reduction zone).[20] Therefore, these results suggest that benthic fluxes of Co are primarily driven by its release at the Mn reduction zone and by its remobilization by both advection and diffusion.

Estimated benthic fluxes of dissolved Ni, Cu, and Cd occurred in both directions (*e.g.*, into and out of the sediment). Most of the estimated diffusive, and all the irrigation-based benthic fluxes, were negative (*i.e.*, into the sediments). This confirms a recent report on the change of direction of net benthic fluxes of Cu and Cd in South Bay.[11] Both sets of estimates suggest these directional variations are due to similarities in the elemental concentrations of surface waters and porewaters and to variations in the inputs and diagenesis of organic material to the sediments.

Benthic Fluxes: Comparison with Riverine Elemental Inputs to the Bay

These few, preliminary, estimates of benthic fluxes were integrated for specific areas to compare with other elemental fluxes to the Bay. For these comparisons, it was conservatively assumed that the estimated diffusive benthic fluxes were representative of the shallower regions (≤ 4 m) of the estuary (232×10^6 m^2 in South Bay and 164×10^6 m^2 in San Pablo Bay).[51] The average riverine input of each dissolved element (Co, Ni, Cu, Zn, and

TABLE IV.

Comparison of previously reported and estimated diffusive benthic fluxes in San Francisco Bay and other saline sediments. Diffusive fluxes in this report were estimated from the average annual concentration in surface waters and the nepheloid or subsurface porewater concentrations, as described in the text. Irrigation fluxes (I) were calculated with the three-zones model of Hammond *et al.*, applying their parameters for a shoal station during summer.[42] The model was not applied to porewater concentration gradients in Coyote Creek and Mayfield Slough, because of the absence of macroorganisms in those sediments.

Location		Co ($\times 10^{-6}$ mol m^{-2} d^{-1})	Ni ($\times 10^{-6}$ mol m^{-2} d^{-1})	Cu ($\times 10^{-6}$ mol m^{-2} d^{-1})	Zn ($\times 10^{-6}$ mol m^{-2} d^{-1})	Cd ($\times 10^{-6}$ mol m^{-2} d^{-1})
Gullmarsfjorden	*D*	0.001				
(Sundby *et al.*, 1986)	*N*	None				
Gullmarsfjorden (Westerlund *et al.*, 1986)	*N*		0.02–0.21	0.03–0.12	1.4–1.9	0.011–0.013
Laurentian Through. (Gobeil *et al.*, 1987)						0.01–0.03
Tyrrhenian Sea (Ciceri *et al.*, 1992)	*D*	0.22–0.37	0.45	–0.02	1.5–6.97	0.004
Tyrrhenian Sea (Ciceri *et al.*, 1992)	*N*	0.10–0.33	–0.11–11.0	–2.4–11.3	18.4–29.4	0.008–0.20
South Bay (Kuwabara *et al.*, 1996)	*N*			–6.5–1.1		–0.3–0.6
Coyote Creek	*n*	0.3	1	0.08	5	–0.001
	1	0.07	0.4	–0.1	7	0.0003
Mayfield Slough	*n*	0.1	1	0.5	7	0.003
	2	0.2	1	0.2	0.8	–0.003
Oakland Harbor	*n*	0.02	0.2	0.001	1	0.003
	1	0.1	0.1	–0.03	0.9	–0.002
	I	0.19	0.11	–0.28	2.0	–0.009
Castro Cove	*n*	0.1	0.6	0.3	5	0.01
	1	0.01	–0.05	–0.05	0.1	–0.001
	I	0.13	0.25	–0.11	5.7	0.008
Inner Castro Cove	*n*	0.01	–0.002	–0.07	0.1	–0.003
	1	0.01	–0.06	–0.03	0.03	–0.001
	I	0.10	–0.12	–0.12	2.1	–0.010
Outer Castro Cove	*n*	0.03	0.03	0.06	0.7	0.002
	1	0.1	0.2	–0.04	0.1	–0.002
	I	0.30	0.10	–0.45	0.9	–0.012
Pinole Point	*n*	0.02	–0.07	–0.09	0.4	0.001
	1	0.2	0.06	–0.04	0.3	–0.002
	I	0.38	–0.19	–0.55	1.0	–0.012

D = Estimated diffusive benthic flux.
N = Measured net benthic flux, by either benthic chambers or core incubation.
n, 1 or 2 = Diffusive benthic flux estimated from the nepheloid layer (n), 1 cm (1) or from 2 cm (2) depth.
I = irrigation plus diffusive fluxes.

Cd) was calculated from concentrations (ng L^{-1}) in the Sacramento and San Joaquin Rivers (Ref. 3, unpublished data) and the corresponding average riverine monthly discharge (L d^{-1}) (M. Ross, personal communication).

As shown in Table V, there appears to be marked differences in the relative amounts of different elemental fluxes in San Francisco Bay waters from

TABLE V.

Comparison between riverine inputs and integrated diffusive fluxes of dissolved elements for shallow areas (0–4 m depth) in San Pablo Bay (164 × 10^6 m^2) and South Bay (232 × 10^6 m^2). The ratios were calculated between the average values of diffusive or net (irrigation plus diffusive) fluxes and average riverine input.

		Co (kg d^{-1})	Ni (kg d^{-1})	Cu (kg d^{-1})	Zn (kg d^{-1})	Cd (kg d^{-1})
Coyote Creek	*n*	3.6	20.1	1.1	77.7	–0.04
	1	1.0	5.2	–1.5	100.7	0.01
Mayfield Slough	*n*	2.0	13.9	7.2	104.3	0.07
	2	2.5	14.9	2.6	12.6	–0.02
Oakland Harbor	*n*	0.3	2.5	0.02	20.5	0.07
	1	1.6	2.0	–0.4	13.4	–0.04
	I	2.6	1.5	–4.1	29.6	–0.24
Castro Cove	*n*	1.4	6.0	3.5	52.6	0.22
	1	0.1	–0.5	–0.5	1.6	–0.02
	I	1.3	2.5	–1.2	61.2	0.14
Inner Castro Cove	*n*	0.1	–0.02	–0.7	1.1	–0.06
	1	0.1	–0.6	–0.4	0.3	–0.02
	I	1.0	–1.1	–1.2	22.1	–0.19
Outer Castro Cove	*n*	0.3	0.3	0.6	7.1	0.04
	1	1.2	1.7	–0.4	1.5	–0.03
	I	2.9	1.0	–4.7	10.1	–0.22
Pinole Point	*n*	0.2	–0.7	–1.0	4.6	0.02
	1	1.9	0.6	–0.4	3.7	–0.03
	I	3.7	–1.8	–5.8	11.1	–0.21
Diffusive fluxes	Minimum	0.1	–0.7	–1.5	0.3	–0.06
	Maximum	3.6	20.1	7.2	104.3	0.22
	Average	1.2	4.7	0.7	28.7	0.01
Irrigation fluxes	Minimum	1.0	–1.8	–5.8	10.1	–0.24
	Maximum	3.7	2.5	–1.2	61.2	0.14
	Average	2.3	0.4	–3.4	26.8	–0.14
Riverine input	Minimum	0.1	8.0	15.4	2.8	0.22
	Maximum	15.4	285.0	290.7	162.8	1.25
	Average	2.4	46.0	68.5	26.4	0.52
Diffusive to Riverine	Ratio	0.48	0.10	0.01	1.1	0.02
Irrigation to Riverine	Ratio	0.95	0.01	–0.05	1.0	–0.28

n = nepheloid layer.
1 or 2 = porewater depth (cm).
I = irrigation plus nepheloid layer fluxes (net benthic fluxes).

sedimentary and fluvial sources. The estimated average diffusive benthic remobilization, or the average irrigation plus diffusion, and the riverine input are of the same magnitude (ratios close to 1) for dissolved Co and Zn. In contrast, benthic remobilization accounts for ≤ 10% of the riverine input of dissolved Ni and only 1 to 2% of the riverine inputs of Cu and Cd in these highly qualified comparisons.

Mass Balance Model: Estimation of Total (Dissolved and Particulate) Benthic Remobilization

A steady-state mass balance model was used to independently estimate the total (dissolved and particulate) benthic remobilization of the different elements in San Francisco Bay sediments (Figure 11). The model included processes for the supply and removal of trace elements to the Bay, which are listed in Table VI. Inputs to the Bay were calculated from fluxes (kg d^{-1}) from the sediment within the estuary (F_{SED}), loads (kg d^{-1}) entering the Bay from point sources (L_i), loads (kg d^{-1}) from atmospheric (A_i) sources, elemental concentrations (kg L^{-1}) in the waters entering the Bay (C_i), and volume (L d^{-1}) of river water moving into the Bay (Q_R) or discharged from point sources (W_i). [Inputs from surface runoff were not included because of insufficient data on those fluxes.] Outputs were calculated from elemental con-

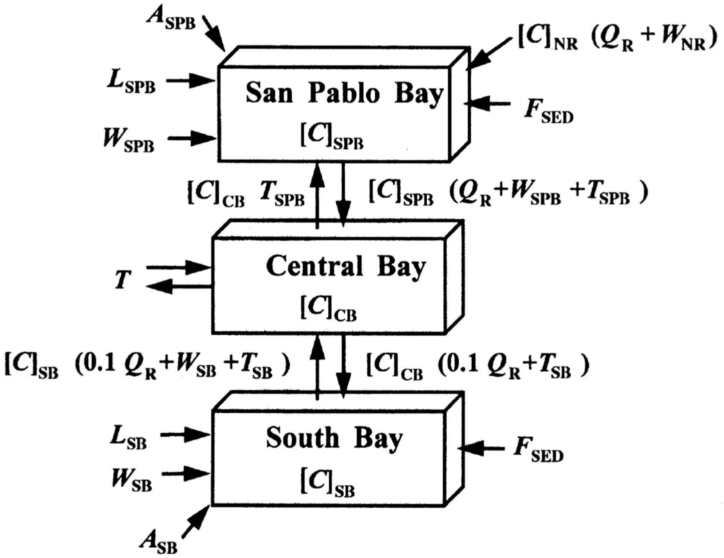

Figure 11. Diagram of the steady-state mass balance models used to estimate the benthic remobilization of trace elements (F_{SED}) in San Pablo and South Bays. The different terms are explained in the text.

centrations (kg L^{-1}) in the water of the Bay (C_o) times the volume (L d^{-1}) of water leaving the Bay, which is equal to the fluvial discharge (Q_R) plus the volume of wastewater discharged to the Bay (W_i) and the volume of

TABLE VI.

Parameters and results of the steady-state mass balance model for total (dissolved and particulate) trace elements in San Francisco Bay.

Northern reach	$[C]_{NR}$				L_{River}
Co_{NR}	8.1×10^{-10} kg L^{-1}				11 kg d^{-1}
Ni_{NR}	5.7×10^{-9} kg L^{-1}				137 kg d^{-1}
Cu_{NR}	5.2×10^{-9} kg L^{-1}				127 kg d^{-1}
Zn_{NR}	8.2×10^{-10} kg L^{-1}				197 kg d^{-1}
Cd_{NR}	5.3×10^{-11} kg L^{-1}				1 kg d^{-1}
Q_R	3.0×10^{10} L d^{-1}				
W_{NR}	1.1×10^{9} L d^{-1}				
San Pablo Bay	$[C]_{SPB}$	L_{SPB}	F_{SED}	A_{SPB}	L_{River}
Co_{SPB}	6.5×10^{-10} kg L^{-1}				11 kg d^{-1}
Ni_{SPB}	5.2×10^{-9} kg L^{-1}	10 kg d^{-1}	509 kg d^{-1}	1 kg d^{-1}	137 kg d^{-1}
Cu_{SPB}	4.0×10^{-9} kg L^{-1}	7 kg d^{-1}	353 kg d^{-1}	6 kg d^{-1}	127 kg d^{-1}
Zn_{SPB}	8.2×10^{-9} kg L^{-1}	15 kg d^{-1}	753 kg d^{-1}	30 kg d^{-1}	197 kg d^{-1}
Cd_{SPB}	8.2×10^{-11} kg L^{-1}	1 kg d^{-1}	0.8 kg d^{-1}	0.2 kg d^{-1}	1 kg d^{-1}
W_{SPB}	2.6×10^{8} L d^{-1}				
T_{SPB}	1.9×10^{11} L d^{-1}				
Central Bay	$[C]_{CB}$				
Co_{CB}	3.8×10^{-10} kg L^{-1}				
Ni_{CB}	2.4×10^{-9} kg L^{-1}				
Cu_{CB}	1.9×10^{-9} kg L^{-1}				
Zn_{CB}	3.0×10^{-9} kg L^{-1}				
Cd_{CB}	7.6×10^{-11} kg L^{-1}				
South Bay	$[C]_{SB}$	L_{SB}	F_{SED}	A_{SPB}	L_{River}
Co_{SB}	6.7×10^{-10} kg L^{-1}				1.1 kg d^{-1}
Ni_{SB}	5.6×10^{-9} kg L^{-1}	40 kg d^{-1}	1296 kg d^{-1}	2 kg d^{-1}	13.7 kg d^{-1}
Cu_{SB}	4.0×10^{-9} kg L^{-1}	46 kg d^{-1}	840 kg d^{-1}	10 kg d^{-1}	12.7 kg d^{-1}
Zn_{SB}	6.2×10^{-9} kg L^{-1}	99 kg d^{-1}	1200 kg d^{-1}	52 kg d^{-1}	19.7 kg d^{-1}
Cd_{SB}	7.6×10^{-11} kg L^{-1}	6 kg d^{-1}	9.7 kg d^{-1}	0.3 kg d^{-1}	0.1 kg d^{-1}
$0.1\ Q_R$	3.0×10^{9} L d^{-1}				
W_{SB}	1.4×10^{9} L d^{-1}				
T_{SB}	4.2×10^{11} L d^{-1}				

$[C]_i$: Respective element total concentration in water of i body of water.
L_{River}: Average river concentration times average river discharge.
Q_R: Average river discharge.
W_i: Wastewater discharge.[10]
L_i: Anthropogenic load.[10]
F_{SED}: Benthic remobilization of total trace elements.
A_i Atmospheric inputs to San Francisco Bay, estimated from deposition rates measured in other parts of the U.S.[52]
T_i: Tidal prism effect (24% of total volume).[17,10]

water moved by the tides (T_i). The inputs and outputs were balanced in the following steady-state equation:

$$F_{\mathrm{SED}} + L_i + A_i + C_i\,(Q_{\mathrm{R}} + W_i) = C_o\,(Q_{\mathrm{R}} + W_i + T_i).$$

The term F_{SED} includes elements coming from different processes, such as benthic remobilization and adsorption-desorption from particles in suspension. This inclusive term was needed to account for the limited information on elemental cycles within the estuary, and is conservatively low because elemental concentrations in Bay waters were measured in leacheates (HCl, $\mathrm{pH} < 2$) of unfiltered samples.

With those qualifications, the equation was used with the data in Table VI to estimate the total (dissolved and particulate) elemental benthic flux in two regions of the estuary. These were San Pablo Bay, which is the largest shallow embayment in the northern reach of the estuary, and the South Bay, which is the shallow embayment in the southern reach of the estuary (Figure 1). The mass-balance was not applied to Co due to the lack of information on loads of this element in point sources discharges and atmospheric sources in San Francisco Bay.

The mass-balance in San Pablo Bay was defined by the following equation:

$$\begin{aligned} F_{\mathrm{SED}} + [C]_{\mathrm{NR}}\,(Q_{\mathrm{R}} + W_{\mathrm{NR}}) + [C]_{\mathrm{CB}}\,T_{\mathrm{SPB}} + L_{\mathrm{SPB}} + A_{\mathrm{SPB}} &= \\ = [C]_{\mathrm{SPB}}\,(Q_{\mathrm{R}} + W_{\mathrm{NR}} + W_{\mathrm{SPB}} + T_{\mathrm{SPB}}) \end{aligned}$$

where inputs of trace elements to San Pablo Bay were based on (i) fluxes from the sediment (F_{SED}); (ii) average total trace element concentrations in the waters of the northern reach from April, 1989 to August, 1994 ($[C]_{\mathrm{NR}}$) (Ref. 3, unpublished data), the mean freshwater discharges of the Sacramento River (Q_{R}) during that period (3.0×10^{10} L d^{-1}; M. Ross, personal communication), and point sources discharges (W_{NR});[10] (iii) point source discharges of trace elements to San Pablo Bay (L_{SPB});[10] (iv) tidal inputs associated with average elemental concentrations ([3] unpublished data) in waters of the Central Bay ($[C]_{\mathrm{CB}}$) considering a tidal exchange (T_{SPB}) of 24% of the total volume of the Bay (7.9×10^{11} L) per day;[17,10] and (v) atmospheric inputs to San Francisco Bay, which were estimated by Gunther *et al.* from deposition rates measured in other parts of the country, and contain a great uncertainty.[52] Outputs from San Pablo Bay were based on average total trace element concentrations in San Pablo Bay ($[C]_{\mathrm{SPB}}$) (Ref. 3, unpublished data) and the volume of water leaving the Bay (from fluvial inputs, wastewater discharges and tidal exchanges). Corresponding fluxes were used to define the mass-balance model for the South Bay, where it was assumed that the fluvial input was 10% of the total river discharge:[10,17]

$$F_{\mathrm{SED}} + [C]_{\mathrm{CB}}\,(0.1\,Q_{\mathrm{R}} + T_{\mathrm{SB}}) + L_{\mathrm{SB}} + A_{\mathrm{SB}} = [C]_{\mathrm{SB}}\,(0.1\,Q_{\mathrm{R}} + W_{\mathrm{SB}} + T_{\mathrm{SB}}).$$

The most important factor regulating the elemental concentration in South Bay waters in this simple model generally was F_{SED} (Table VI). In general, F_{SED} was also two- to ten-fold lower in San Pablo Bay than in South Bay. In San Pablo Bay, F_{SED} was the most important term for Ni, Cu, and Zn in comparison to point sources (L_{SPB}), atmospheric (A_{SPB}), and riverine (L_{River}) inputs. Only in San Pablo Bay was the F_{SED} of Cd similar to both L_{SPB} and L_{River}. While these results indicate that benthic remobilization and adsorption-desorption from suspended particles may be the most important factors regulating the concentration of trace elements in the waters in both San Pablo Bay and the South Bay, it must be reemphasized that these simple models ignore the undefined, but potentially very important, fluxes from surface runoff.

Resuspension Load

Resuspension loads were independently calculated from sediment resuspension and particulate elemental concentrations. Fuller estimated the sediment resuspension for shallow areas of both San Pablo Bay (1.1 g cm^{-2} yr^{-1}) and South Bay (0.7 g cm^{-2} yr^{-1}).[51] These resuspension rates were used in conjunction with near-total elemental concentrations (Figure 7) to calculate

TABLE VII.

Resuspension loads of trace elements in San Francisco Bay. These loads were calculated from the sediment resuspension rates for shallow areas in the Bay[51] and the near-total elemental concentrations (Figure 7) measured in surficial sediments. The ratios are given between the benthic fluxes (F_{SED}) calculated from the mass-balance models (Table VI) and the calculated resuspension loads.

	Co		Ni		Cu		Zn		Cd	
	Load (kg d^{-1})	Ratio (%)	Load (kg d^{-1})	Ratio (%)	Load (kg d^{-1})	Ratio (%)	Load (kg d^{-1})	Ratio (%)	Load (kg d^{-1})	Ratio (%)
South Bay										
Coyote Creek	90	–	531	41	220	26	1549	129	3.6	37
Mayfield Slough	126	–	795	61	334	40	1022	85	1.4	14
Oakland Harbor	119	–	705	54	712	85	1779	148	3.3	34
San Pablo Bay										
Castro Cove	115	–	691	136	388	110	911	121	2.7	340
Inner Castro Cove	113	–	670	132	841	238	964	128	3.2	400
Outer Castro Cove	95	–	461	91	313	89	727	97	1.7	210
Pinole Point	97	–	467	92	274	78	632	84	1.3	160

– : Not computable due to insufficient data.

the load due to resuspension of surficial sediments (Table VII), which is equivalent to F_{SED}, as obtained with the mass-balance models. For these calculations, it was assumed that the resuspension rate was similar to the whole embayment and the areas were those defined by Fuller.[51]

These calculations suggest resuspension loads are similar in magnitude to the total (dissolved and particulate) benthic fluxes (F_{SED}). The ratios of F_{SED} to resuspension loads (Table VII) are lower (14 to 148%) in the South Bay than in San Pablo Bay (78 to 400%), which corresponds with their estimated variations in sediment resuspension.[51] While there was an anomalously large range in the ratio for Cd (14 to 400%), there were relatively narrow ranges in the other ratios (Ni 41 to 136%, Cu 26 to 238%, Zn 84 to 148%). This indicates the resuspension load could be one fourth to two-times the values calculated in the preceding mass-balance models and it corroborates the magnitude of the total benthic fluxes (F_{SED},) calculated with the mass balance models. Furthermore, the similarities in these independent estimations attest to the relative importance of benthic remobilization in controlling elemental concentrations in San Francisco Bay.

CONCLUSIONS

Benthic remobilization is an important source of trace elements to surface waters of San Francisco Bay. The release of trace elements to porewaters is regulated by the degradation of organic matter in oxic and suboxic zones, the reduction of Mn in suboxic zones, and the formation of metal-sulfide soluble complexes in anoxic zones. Once the elements are dissolved in the porewater they can be transported out of the sediment by diffusion and advection. Calculations of the estimated diffusive benthic remobilization indicate they are comparable to the riverine inputs of Co and Zn to the estuary, but they are an order of magnitude less than the riverine inputs of Ni, Cu, and Cd. Two independent complementary calculations on the total (dissolved and particulate) benthic flux (including diagenetic remobilization, resuspension and adsorption-desorption processes) indicate that it is greater than either riverine, point source, or atmospheric inputs of Ni, Cu, Zn, and Cd to San Francisco Bay. These analyses corroborate previous studies which indicate the importance of benthic fluxes as source of elements to waters in the estuary.[8,11] All of these studies also substantiate the proposal that benthic remobilization will become a relatively greater source of elements to surface waters of enclosed embayments as inputs from point sources and surface runoff are reduced.[7]

Acknowledgments. – We appreciate the valuable comments from Margaret Delaney, Robert Garrison, Joris Gieskes and two anonymous reviewers. This work was supported by the California State Research Contrôl Board, and the Minerals Management Service, and the University of California President's Dissertation-Year Fellowship Program.

REFERENCES

1. A. R. Flegal, I. Rivera-Duarte, P. I. Ritson, G. M. Scelfo, G. J. Smith, M. R. Gordon, and S. A. Sañudo-Wilhelmy, *Metal contamination in San Francisco Bay waters: Historic perturbations, contemporary concentrations, and future considerations*, in: J. T. Hollibaugh (Ed.), *San Francisco Bay: The Ecosystem*, Pac. Div. Amer. Assoc. Advance Sci., San Francisco, CA, 1996, pp. 173–188.
2. R. M. Gordon, *Trace element concentrations in seawater and suspended particulate matter from San Francisco Bay and adjacent coastal waters.* M. S. Thesis, San Jose State University, 1980, pp. 85.
3. A. R. Flegal, G. J. Smith, G. A. Gill, S. Sañudo-Wilhelmy, and L. C. D. Anderson, *Mar. Chem.* **36** (1991) 329–363.
4. G. J. Smith and A. R. Flegal, *Estuaries* **16** (1993) 547–558.
5. K. E. Abu-Saba and A. R. Flegal, *Mar. Chem.* **49** (1995) 189–199.
6. D. A. Wright and D. J. H. Phillips, *Mar. Poll. Bull.* **19** (1988) 405–413.
7. A. R. Flegal and S. A. Sañudo-Wilhelmy, *Environ. Sci. Technol.* **27** (1993) 1934–1936.
8. I. Rivera-Duarte and A. R. Flegal, *Geochim. Cosmochim. Acta* **58** (1994) 3307–3313.
9. T. M. Wood, A. M. Baptista, J. S. Kuwabara, and A. R. Flegal, *Limnol. Oceanogr.* **40** (1995) 345–358.
10. J. A. Davis, A. J. Gunther, B. J. Richardson, J. M. O'Connor, R. B. Spies, E. Wyatt, E. Larson and E. M. Meiorin, *Status and trends report on pollutants in the San Francisco Bay estuary.* San Francisco Bay- Delta Aquatic Habitat Institute, Richmond, CA, 1991, pp. 240.
11. J. S. Kuwabara, C. C. Y. Chang, A. I. Khechfe, and Y. R. Hunter, *Importance of dissolved sulfides and organic substances in controlling the chemical speciation of heavy metals in San Francisco Bay*, in: J.T. Hollibaugh (Ed.), *San Francisco Bay: The Ecosystem*, Pac. Div. Amer. Assoc. Advance Sci., San Francisco, CA, 1996, pp. 157–172.
12. I. Rivera-Duarte and A. R. Flegal, 1997, manuscript in preparation,
13. R. A. Jahnke, *Limnol. Ocean.* **33** (1988) 483–487.
14. K. W. Bruland, K. H. Coale, and L. Mart, *Mar. Chem.* **17** (1985) 285–300.
15. I. Rivera-Duarte and A. R. Flegal, *Anal. Chim. Acta* **328** (1996) 13–17.
16. A. R. Flegal, L. S. Cutter, and J. H. Martin, *A study of the chemistry of marine sediments and wastewater sludge.* Cal. State Wat. Res. Control Board, 1981, pp. 69.
17. T. J. Conomos, *Properties and circulation of San Francisco Bay waters*, in: T. J. Conomos, A. E. Leviton, and M. Berson (Eds.), *San Francisco Bay: the urbanized estuary.* Pac. Div. Amer. Assoc. Advance Sci., 1979, pp. 47–84.
18. G. Ciceri, S. Maran, W. Martinotti, and G. Queirazza, *Hydrobiologia* **235/236** (1992) 501–517.
19. S. F. G. Westerlund, L. G. Anderson, P. O. J. Hall, Å. Iverfeldt, M. M. Rutgers Van Der Loeff, and B. Sundby, *Geochim. Cosmochim. Acta* **50** (1986) 1289–1296.
20. B. Sundby, L. G. Anderson, P. O. Hall, Å. Iverfeldt, M. Rutgers Van Der Loeff, and S. F. G. Westerlund, *Geochim. Cosmochim. Acta* **50** (1986) 1281–1288.
21. T. J, Shaw, J. M. Gieskes, and R. A. Jahnke, *Geochim. Cosmochim. Acta* **54** (1990) 1233–1246.
22. A. Nissenbaum and D. J. Swaine, *Geochim. Cosmochim. Acta* **40** (1976) 809–816.

23. H. Kerndorff and M. Schnitzer, *Geochim. Cosmochim. Acta* **44** (1980) 1701–1708.
24. S. Emerson, L. Jacobs, and B. Tebo, *The behavior of trace metals in marine anoxic waters: solubilities at the oxygen-hydrogen sulfide interface*, in: C. S. Wong, E. A. Boyle, K. W. Bruland, J. Burton and E. D. Goldberg (Eds.), *Trace Metals in Sea Water*. NATO Mar. Sci. Serv., 9. Plenum Press, New York, NY, 1983, pp. 579–608.
25. J.A. Davis, *Geochim. Cosmochim. Acta* **48** (1984) 679–691.
26. K. Fischer, J. Dymond, M. Lyle, A. Soutar, and S. Rau, *Geochim. Cosmochim. Acta* **50** (1986) 1535–1543.
27. H. Elderfield, *Amer. J. Sci.* **281** (1981) 1184–1196.
28. D. J. Burdige, S. A. Skrabal, and J. R. Donat, *The speciation of copper in bottom waters and pore waters of Chesapeake Bay and Atlantic coastal waters: Implications for sediment-water exchange*, Amer. Geophys. U., December 5–9, San Francisco, CA, 1994, abstract.
29. L. W. Lion, R. S. Altmann, and J. O. Leckie, *Environ. Sci. Technol.* **16** (1982) 660–666.
30. J. S. Kuwabara, C. C. Y. Chang, J. E. Cloern, T. L. Fries, J. A. Davis, and S. N. Luoma, *Est. Coast. Shelf Sci.* **28** (1989) 307–325.
31. J. R. Donat, K. A. Lao, and K. W. Bruland, *Anal. Chim. Acta* **284** (1994) 547–571.
32. K. K. Turekian, *Geochim. Cosmochim. Acta* **41** (1977) 1139–1144.
33. L. Jacobs, S. Emerson, and J. Skei, *Geochim. Cosmochim. Acta* **49** (1985) 1433–1444.
34. M. Öztürk, *Mar. Chem.* **48** (1995) 329–342.
35. P. H. Santschi, M. Amdurer, D. Adler, P. O'Hara, Y.-H. Li, and P. Doering, *J. Mar. Res.* **45** (1987) 1007–1048.
36. J. J. Sawlan and J. W. Murray,. *Earth Planet. Sci. Let.* **64** (1983) 213–230.
37. W. Stumm and J. J. Morgan, *Aquatic Chemistry*. 2nd. edition, John Wiley & Sons, New York, N.Y., 1981, pp. 780.
38. J. Boulègue, *Trace metals (Fe, Cu, Zn, Cd) in anoxic environments,* in: C. S. Wong, E. A. Boyle, K. W. Bruland, J. Burton and E. D. Goldberg (Eds.), *Trace Metals in Sea Water*. NATO Mar. Sci. Ser., 9. Plenum Press, New York, NY, 1983, pp. 563–577.
39. W. B. Lyons and W. F. Fitzgerald, *Trace metals speciation in nearshore anoxic and suboxic pore waters*, in: C. S. Wong, E. A. Boyle, K. W. Bruland, J. Burton and E. D. Goldberg (Eds.), *Trace Metals in Sea Water*. NATO Mar. Sci. Ser., 9. Plenum Press, New York, NY, 1983, pp. 621–641.
40. C. Gobeil, N. Silverberg, B. Sundby, and D. Cossa, *Geochim. Cosmochim. Acta* **51** (1987) 589–596.
41. J. S. Kuwabara and G. W. Luther, III. *Estuaries* **16** (1993) 567–573.
42. D. E. Hammond, C. Fuller, D. Harmon, B. Hartman, M. Korosec, L. G. Miller, R. Rea, S. Warren, W. Berelson, and S. W. Hager, *Hydrobiol.* **129** (1985) 69–90.
43. N. Iversen and B. B. Jørgensen, *Geochim. Cosmochim. Acta* **57** (1993) 571–578.
44. J. M. Caffrey, B. E. Cole, J. E. Cloern, J. R. Rudek, A. C. Tyler, and A. D. Jassby, *Studies of the San Francisco Bay, California, Estuarine Ecosystem.* Pilot regional monitoring results, 1993. U. S. Geol. Surv., Open File Report 94–82, Menlo Park, CA, 1994, pp. 412.
45. M. M. Rutgers van der Loef, L. G. Anderson, P. O. J. Hall, Å. Iverfeldt, A. B. Josefson, B. Sundby, and S. F. Westerlund, *Limnol. Oceanogr.* **29** (1984) 675–686.
46. A. Tessier, R. Carignan, and N. Belzile, *Processes occurring at the sediment-water interface: Emphasis on trace elements*, in: J. Buffle and R. R. De Vitre (Eds.), *Che-*

mical and Biological Regulation of Aquatic Systems, Lewis, Boca Raton, Florida, 1994, pp. 137–173.

47. S. Emerson, R. Jahnke, and D. Heggie, *J. Mar. Res.* **42** (1984) 709–730.
48. P. Santschi, P. Höhener, G. Benoit, and M. Buchholtz-ten Brink, *Mar. Chem.* **30** (1990) 269–315.
49. R. C. Aller and J. Y. Aller, *Limnol. Oceanogr.* **37** (1992) 1018–1033.
50. J. M. Caffrey, D. E. Hammond, J. S. Kuwabara, L. G. Miller, and R. R. Twilley, *Benthic processes in South San Francisco Bay: The role of organic inputs and bioturbation*, in: J. T. Hollibaugh (Ed.), *San Francisco Bay: The Ecosystem*, Pac. Div. Amer. Assoc. Advance Sci., San Francisco, CA, 1996, pp. 425–442.
51. C. C. Fuller, *The Use of Pb-210, Th-234 and Cs-137 as Tracers of Sedimentary Processes in San Francisco Bay,, California*. M. S. Thesis, University of Southern California, 1982, 251 pp.
52. A. J. Gunther, J. A. Davis, and D. J. H. Phillips, *An assessment of the loading of toxic contaminants to the San Francisco Bay Delta*. Aquatic Habitat Institute, Richmond, CA, 1987, pp. 330.
53. D. C. McCorkle and G. P. Klinkhammer, *Geochim. Cosmochim. Acta* **55** (1991) 161–168.

SAŽETAK

Gradijenti u vodama pora sedimenata i difuzijski bentički fluksovi Co, Ni, Cu, Zn i Cd u zaljevu San Francisca

Ignacio Rivera-Duarte i A. Russell Flegal

Da bi se odredila remobilizacija Co, Ni, Cu, Zn i Cd iz sedimenata, izmjereni su gradijenti koncentracije otopljenog (< 0,45 µm) i partikularnog u relativno nezagađenim i u kontaminiranim sedimentima zaljeva San Francisca, kao i u relativno nezagađenim susjednim uvalama (Tomales i Drakes Estero). Utvrđeno je da dijagenetsko otpuštanje ovih elemenata u intersticijske vode reguliraju tri mehanizma: (i) raspad organske tvari u oksičnim i suboksičnim zonama; (ii) redukcija Mn u suboksičnim zonama; i (iii) nastajanje topljivih metala sulfidnih kompleksa u anoksičnim zonama. Dok su procijenjeni difuzijski bentički fluksovi Ni, Cu i Cd bili relativno maleni (≤ 10%) u usporedbi sa riječnim fluksovima, procijenjeni difuzijski fluksovi Co i Zn slični su (≈ 100%) njihovim riječnim unosima. Te preliminarne procjene također pokazuju da cjelokupna (otopljena i partikularna) remobilizacija Co, Ni, Cu i Zn premašuje unose i riječnih i točkastih izvora tih elemenata u zaljevu San Francisca. Štoviše, moguće je predvidjeti da ti bentički unosi mogu postati znatni kad se budu smanjili antropogeni unosi tih elemenatza iz točkastih i ostalih izvora.