

Synthesis of long-term nickel monitoring in San Francisco Bay[☆]

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Abstract

The Regional Monitoring Program for Water Quality in the San Francisco Bay (RMP) has conducted annual monitoring of the San Francisco Estuary (estuary) since 1993. The RMP primarily monitors water, sediment, and bivalves, although short-term pilot and special studies on select topics are also conducted. The purpose of this article is to synthesize over 10 years of RMP nickel data and to illustrate how comprehensive monitoring data contribute to an understanding of contaminant fate. Nickel concentrations observed in water (43.7–233.7 nM) are largely a function of the geology of the watershed surrounding the estuary and inputs from wastewater treatment plants and urban runoff. The geologic formations supplying sediment to the estuary contain high concentrations of nickel (e.g., 1000–3300 µg/g). Much of the research to date on nickel speciation suggests that nickel complexes from wastewater treatment plants are not readily available for biological uptake [Bedsworth, W.W., Sedlak, D.L., 1999. Sources and environmental fate of strongly complexed nickel in estuarine waters: the role of ethylenediaminetetraacetate. *Environ. Sci. Technol.* 33, 926–931, Sedlak, D.L., Phinney, J.T., Bedsworth, W.W., 1997. Strongly complexed Cu and Ni in wastewater effluents and surface runoff. *Environ. Sci. Technol.* 31(10), 3010–3016, Donat, J.R., Lao, K.A., Bruland, K.W., 1994. Speciation of dissolved copper and nickel in South San Francisco Bay: a multi-method approach. *Anal. Chim. Acta.* 284, 547–571]. In addition, concentrations of nickel measured in biota by the RMP (0.905–113.0 µg/g dry weight in bivalve tissues) are well below recommended maximum tissue residue levels (220 µg/g wet weight, California state guidelines). Based on this information, regulators have reconsidered the water quality objectives developed for nickel. © 2007 Elsevier Inc. All rights reserved.

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1. Introduction

Nickel is a trace element that is abundant in serpentine minerals and industrial products (Parker, 1967; Bailey and Everhart, 1964; Oze et al., 2004; Himmelberg and Coleman, 1968). Although nickel is not particularly toxic to humans, certain species of aquatic organisms are susceptible to nickel toxicity, leading USEPA to issue water quality criteria for the protection of aquatic life (USEPA, 1976). The four most sensitive saltwater genera listed in the 1976 criteria document were *Heteromysis* (shrimp), *Merccenaria* (clam), *Mysidopsis* (shrimp), and *Crassostrea* (oyster), with subsequent updates resulting in slight changes in

the most sensitive species. More recent work (Hunt and Anderson, 2002) has identified sensitive *Mysidopsis* and *Haliotis* (abalone) species whose inclusion in derivation of the national water quality criteria would decrease the acute (criterion maximum concentration, CMC) criterion for nickel, but increase the criterion continuous concentration (CCC), which is always the lower of the two criteria.

In the mid-1990s, nickel concentrations in the lower South San Francisco Bay frequently exceeded the total recoverable based marine water quality objectives established for the protection of aquatic life specified in the National Toxics Rule (CEP, 2005a). These exceedances resulted in this portion of the estuary being listed on the State of California's Clean Water Act 303 (d) list of impaired water bodies. In addition to nickel, copper, mercury, and selenium were also identified in 1998 as impairing beneficial uses of the South San Francisco Bay. Inclusion on the 303 (d) list requires the San Francisco

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Regional Water Quality Control Board (SFRWQCB) to develop Total Maximum Daily Loads (TMDL) for each of the trace elements. TMDLs are calculated for both non-point sources and point sources of pollution to the surface water. As part of the TMDL process, studies were undertaken to understand the sources and fate of copper and nickel in the estuary and to develop a range of scientifically defensible water quality objectives for nickel and copper based on the bioavailable dissolved metal fraction. The results have been Basin Plan Amendments that have established site-specific objectives for these elements for Lower South San Francisco Bay. In January 2004, the SFRWQCB approved amendments to the Water Quality Control Plan (Basin Plan, SFRWQCB, 2004) that replaced the total recoverable metals based water quality objectives (WQOs) in the 1995 Basin Plan with the updated dissolved metals based WQOs (Table 1) from the California Toxics Rule (USEPA, 2000).

Extensive monitoring has been conducted in San Francisco Bay to describe the distribution and trends of pollutant concentrations. The Regional Monitoring Program for Water Quality (RMP), administered by the San Francisco Estuary Institute, has conducted annual monitoring of the estuary since 1993. This monitoring has primarily consisted of annual water, sediment, and bivalve sampling, although short-term pilot and special studies are also conducted. Until 2002, this sampling was conducted in both the wet (November to May) and dry (June to October) seasons with a fixed station design. In 2002, the RMP implemented a randomized design for distribution of sampling locations to representatively characterize more of the estuary. At that time, it was decided to sample only in the dry season when there is reduced seasonal variation due to the lack of major storm events during the summer.

The RMP data are used for a multitude of purposes including developing TMDLs and National Pollutant Discharge Elimination System (NPDES) permits; evaluating impairment of the estuary (i.e., diminished beneficial uses) and subsequent inclusion or removal from the Clean

Water Act 303 (d) impaired water body list; and improving our understanding of pollutant loadings and other processes within the estuary (Tetra Tech, 1999 and SFEI, 2006).

The purpose of this article is to synthesize information from various sources with 10 years of data collected by the RMP and to illustrate how comprehensive monitoring data contribute to an understanding of contaminant fate. By comparing monitoring data with information on nickel sources, speciation and toxicity, regulators have been able to develop effective approaches for protecting San Francisco Bay.

2. Water

Since 1993, the RMP has measured aqueous concentrations of several trace metals including nickel (SFEI, 2005). Over this 10-year period, between 22 and 31 stations have been sampled annually during the wet and dry seasons. Surface water samples (~1 m depth) were collected using a peristaltic pump system. The water samples for dissolved nickel analyses were obtained using an acid-cleaned polypropylene filter cartridge (0.45 µm pore size). The unfiltered water samples for total nickel analyses were pumped directly into acid-cleaned containers. Both unfiltered samples for recoverable “near-total” nickel analyses (hereafter referred to as “total” nickel) and filtered samples for dissolved nickel were acidified to pH~1.8 with hydrochloric acid. Samples collected prior to 2000 were analyzed using liquid–liquid organic extraction and graphite furnace atomic absorption spectrometry (GFAAS). Beginning in 2000, samples were analyzed using on-line chelating resin column partitioning with inductively coupled plasma-mass spectrometry, (CRCP-ICP-MS) (Ndung'u et al., 2003; Beck et al., 2002a).

The City of San Jose Environmental Services Department has conducted long-term monitoring of trace metals in South San Francisco Bay (San Jose, 2004) since 1997. The City's monitoring program has included bi-monthly or monthly sampling at 12 locations. Data from over 1000 measurements collected between 1997 and 2005 are presented in this paper. The data collection procedures were based on the RMP-program methods and are comparable. Multiple extraction methods were utilized during the course of the sampling program, and both GFAAS and ICP-MS analysis methods were used.

2.1. Spatial and temporal trends

Summary statistics for total nickel and dissolved nickel concentrations in the five main regions of the Bay (see Fig. 1 for locations), based on over 1500 measurements, are presented in Table 2. The average values for measurements made in the Pacific Ocean near the Golden Gate Bridge are presented for comparison, where salinity ranged from 31 to 33 practical salinity units (psu) in the dry season and as low as 23 psu in the wet season.

Table 1
Aquatic life water quality objectives

	CCC 4-Day average µg/L (µmol/L)	CMC 1-h average µg/L (µmol/L)
Dissolved freshwater water quality objective	52 (0.9)	470 (8)
Dissolved marine water quality objective ^a	8.2 (0.1)	74 (1.3)
Dissolved site-specific objective for south of Dumbarton Bridge ^b	11.9 (0.2)	62.4 (1.1)

Source: San Francisco Basin Plan (San Francisco Regional Water Quality Control Board, www.waterboards.ca.gov/rwqcb2/basinplan.htm).

^aMarine Water Quality Objective is applicable to sites where salinity is greater than 10 parts per thousand 95% of the time.

^bThis objective is applicable to the portion of the estuary south of the Dumbarton Bridge.

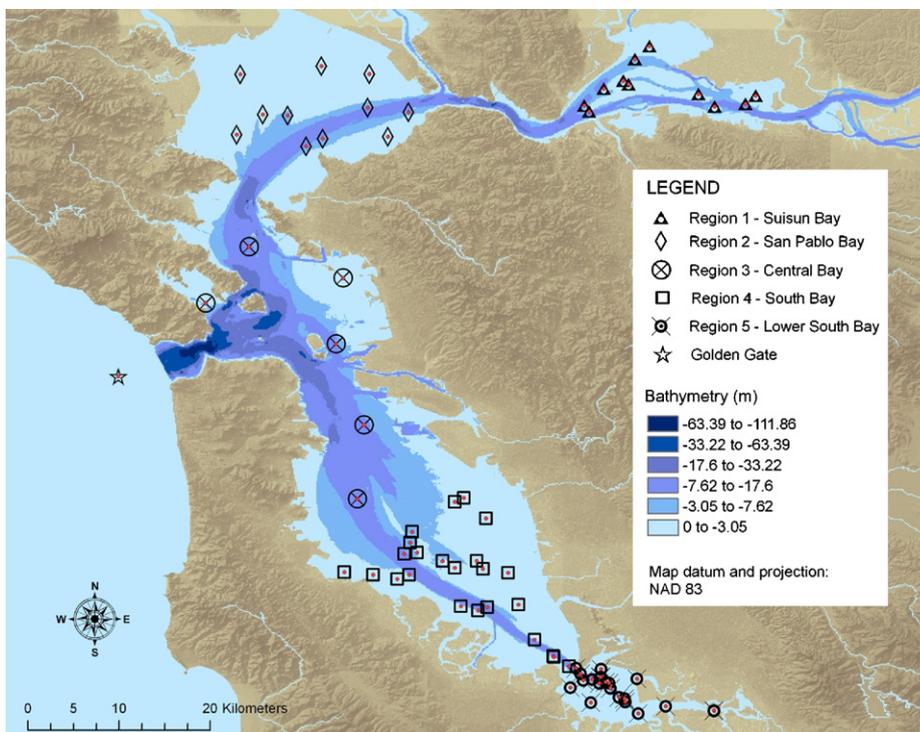


Fig. 1. Location of RMP water sampling sites in five regions of San Francisco Estuary. All sites were sampled in a similar manner and were included in the statistical analyses conducted. Further details regarding individual sample cruises and methods can be found in the RMP Annual Monitoring Results report for each year (http://www.sfei.org/rmp/rmp_docs.html) and the City of San Jose's website (<http://www.sanjoseca.gov/esd/PDFs/SBReport2003.pdf>).

The highest average concentrations of both total nickel (13.7 $\mu\text{g/L}$, 233 nM) and dissolved nickel (4.0 $\mu\text{g/L}$, 68 nM) occurred in Lower South San Francisco Bay (Region 5), where 15% of the total nickel measurements exceeded 19.8 $\mu\text{g/L}$ (337 nM). Total nickel concentrations in Suisun Bay and San Pablo Bay (Region 2) were the next highest with average concentrations approximately 8 $\mu\text{g/L}$ (136 nM) or 60% of the average concentration measured in Lower South San Francisco Bay. As the result of tidal mixing and exchange with the near-shore coastal waters, the lowest nickel concentrations in both the total (2.6 $\mu\text{g/L}$ or 44.3 nM) and dissolved phase (1.3 mg/L or 22.1 nM) occurred in the Central Bay (Region 3).

Total nickel concentrations in all five regions of the bay are strongly influenced by the suspended sediment concentrations. The values of the product-moment correlation coefficient (r) for paired measurements of total suspended solids (TSS) and total nickel concentrations throughout the bay were 0.91 and 0.90 in the dry and wet seasons, respectively. The values for the correlation coefficient in the dry season ranged from 0.74 to 0.94, and the range of correlation coefficients for the wet season was 0.84–0.91. The correlations calculated bay-wide and regionally for total nickel and TSS concentrations were statistically significant in all cases ($p \leq 0.05$).

Dissolved nickel concentrations were less strongly influenced by episodic resuspension of sediments, and the correlations between TSS and dissolved nickel concentrations were lower and more variable within regions. The

values of bay-wide correlation coefficients were 0.27 and 0.22 for the dry and wet seasons, respectively. The range of the r values for the dry season was -0.32 to 0.41 , and -0.05 to 0.39 for the wet season. Fewer than half of the computed correlation coefficients for the wet season were statistically significant. The primary inputs of dissolved nickel to the water column are remobilization via resuspension and desorption from benthic sediments, benthic diffusive fluxes, and discharges from wastewater treatment facilities (Topping and Kuwabara, 2003; Tetra Tech, 1999).

The average total nickel and dissolved nickel concentrations measured in the dry-weather season over a 13-year period (1993–2005) are presented in Fig. 2. The highest average total and dissolved nickel concentrations each year were almost always measured in Lower South San Francisco Bay (Region 5). In all five regions, total nickel concentrations were highly variable, due to the correlation between total nickel and TSS concentrations and the large variations in TSS concentrations among samples.

The influence of TSS concentrations on total nickel concentrations was clearly evident in Lower South San Francisco Bay (Region 5) between 1997 and 2005, where up to 48 samples were collected at individual stations annually by the City of San Jose. Between 1997 and 2001 a high proportion of the samples were intentionally collected at extreme low- and high-tide levels. The average TSS concentrations ranged between 86 and 191 mg/L, and the average total nickel concentrations ranged between 12 and

Table 2
Summary statistics for total and dissolved nickel concentrations ($\mu\text{g/L}$) measured in San Francisco Bay (1998–2005)

Region	Average all data		Average dry season		Average wet season	
	Total Ni (<i>n</i> , min–max, CV)	Dissolved Ni (<i>n</i> , min–max, CV)	Total Ni (<i>n</i> , min–max, CV)	Dissolved Ni (<i>n</i> , min–max, CV)	Total Ni (<i>n</i> , min–max, CV)	Dissolved Ni (<i>n</i> , min–max, CV)
1-Suisun	8.1 (80, 2–28, 0.58)	1.5 (80, 1–5, 0.44)	7.6 (34, 3–24, 0.52)	1.3 (34, 1–2, 0.25)	8.5 (46, 2–28, 0.61)	1.6 (46, 1–5, 0.48)
2-San Pablo	8.0 (83, 2–36, 0.88)	1.7 (83, 1–4, 0.32)	6.3 (35, 2–20, 0.66)	1.6 (35, 1–2, .15)	9.3 (48, 2–36, 0.83)	1.8 (48, 1–4, 0.39)
3-Central	2.6 (153, 1–7, 0.47)	1.3 (153, 1–2, 0.30)	2.4 (61, 1–7, 0.46)	1.2 (61, 1–2, 0.23)	2.7 (92, 1–7, 0.47)	1.4 (92, 1–2, 0.32)
4-South	5.2 (195, 1–24, 0.58)	2.5 (206, 1–4, 0.25)	4.9 (103, 1–12, 0.42)	2.6 (107, 1–4, 0.24)	5.6 (92, 2–24, 0.68)	2.4 (99, 1–3, 0.24)
5-Lower South	13.7 (1065, 2–210, 1.18)	4.0 (1115, 2–13, 0.35)	14.5 (574, 3–211, 1.27)	4.4 (575, 2–13, 0.31)	12.9 (491, 2–133, 1.03)	3.6 (540, 2–10, 0.38)
Delta	4.5 (54, 1.8–22, 0.67)	1.3 (54, 0.7–3.2, 0.44)	3.5 (22, 1.8–5.3, 0.29)	1.0 (21, 0.7–1.3, 0.19)	5.1 (32, 1.8–22, 0.72)	1.5 (33, 0.7–3.2, 0.43)
Golden Gate	0.8 (23, 0.3–2, 0.44)	0.6 (23, 0.3–1, 0.36)	0.6 (10, 0.3–1, 0.46)	0.5 (10, 0.3–1, 0.24)	0.9 (13, 0.3–2, 0.35)	0.7 (13, 0.3–1, 0.46)

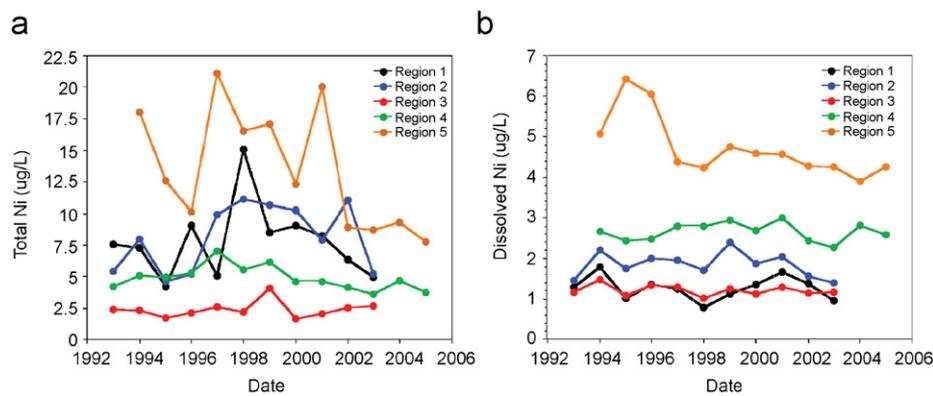


Fig. 2. Average total (a) and dissolved (b) nickel concentrations (mg/L) in five regions of San Francisco Bay 1993–2005. The graphic includes both RMP and City of San Jose data.

$21 \mu\text{g/L}$ ($204\text{--}358 \text{ nM}$). Beginning in 2002, the sampling regime was modified so that the samples were collected throughout the tidal range. The average TSS concentration in this period ranged between 43 and 56 mg/L , with a corresponding drop in average total nickel concentrations to between 8 and $9 \mu\text{g/L}$ ($136\text{--}153 \text{ nM}$).

Differences were found between the other four regions of San Francisco Bay (Fig. 2) in both total nickel and dissolved nickel concentrations. For example, the average total nickel concentrations in Suisun Bay (Region 1) approximately equaled or in some years exceeded the average concentrations in San Pablo Bay (Region 2), but the average dissolved nickel concentration measured in Suisun Bay was significantly ($p \leq 0.05$) lower than in San Pablo Bay. Flegal et al. (1991) previously noted that the dissolved concentrations of several trace elements including nickel exhibit non-conservative increases in the northern reaches of the estuary, indicating within-segment sources or transformation processes. Mean concentrations of total

and dissolved nickel concentrations in Lower South San Francisco Bay were significantly ($p \leq 0.05$) and substantially (about two-fold or more) greater than all other regions, with the highest concentrations measured in the dry season.

There are often also differences between the wet (November–May) and dry (June–October) seasons within each region for both total and dissolved nickel concentrations (Table 2). In Suisun, San Pablo, and Central Bays, average concentrations of both total and dissolved nickel were greater in the wet season, although the seasonal differences were significant only for the dissolved phase in Suisun and Central Bays and for total nickel in San Pablo Bay. In contrast, average dissolved nickel in South and Lower South Bays were higher in the dry season. This may be attributed to the fact that the North Bay nickel input is dominated by wet-weather inflow, whereas in the South Bay in the drier summer months, the freshwater flow into the Bay is dominated primarily by effluent discharge (Squire et al., 2002; Conomos, 1979).

2.2. Nickel sources and loadings—mass balance for lower South San Francisco Bay

Based on average concentrations (measured by RMP) and calculated flows from the Sacramento–San Joaquin Delta (from the California Department of Water Resources), the primary source of total and dissolved nickel is riverine input in the northern reach of the estuary (Region 1). Flegal et al. (1991) had noted non-conservative distributions of dissolved nickel and other trace elements concentration gradients in the northern reach of the estuary. By applying measured groundwater seepage and bioirrigation rates to pore water dissolved nickel concentrations, Spinelli et al. (2002) found that less than 4% of the unknown sources of dissolved nickel could be accounted for by benthic fluxes. Flegal et al. (2005) attributed the observed increases in dissolved nickel concentrations between the Sacramento/San Joaquin Rivers and the Pacific Ocean to natural processes (e.g., diagenic remobilization of trace elements in benthic sediments) or anthropogenic processes (e.g., wastewater discharges).

As shown in the summary statistics in Table 2, large differences in both total and dissolved nickel concentrations exist between the northern (Region 1) and southernmost (Region 5) reaches of San Francisco Bay. These differences have been attributed to both the large disparity in volumes of natural freshwater flows into the northern (~90%) and southern (~10%) regions of the estuary, which accounts for the pronounced differences in contaminant residence times between those two regions, and the differences in the trace metal sources. Flegal et al. (2005) reported that 76% of the total publicly owned treatment works (POTW) effluent released into San Francisco Bay enters the shallow waters of the southern region, and only 20% enters the waters of the northern region.

A detailed evaluation of the source of nickel in the Lower South Bay (Region 5) was calculated to support the San Francisco Regional Water Quality Control Board's TMDL regulatory program. Details of the model developed to estimate total copper and nickel fluxes for both the dry and wet seasons were reported by Tetra Tech (1999). First, the dry season total copper flux past the Dumbarton Bridge (boundary between Regions 5 and 4) was calculated using an estimated residence time in Region 5, concentrations at reference stations in Region 5 and north of the Dumbarton Bridge, and the volume of Lower South Bay. Results from hydrodynamic modeling (Gross, 1997) provided estimates of retention time (20 days). The particulate flux of copper from the bed was calculated as the difference in the total flux past the Dumbarton Bridge minus the total of external loads of copper to Lower South Bay from all sources (point, atmospheric, tributaries and diffusive flux). The dry season particulate flux of nickel from the bed was then calculated using the ratio of nickel to copper in the bed. Wet season particulate copper flux

was then derived from dry season flux previously calculated, adjusted for relative suspended particulate and particulate copper concentrations in wet and dry seasons. Particulate nickel flux was then calculated from the ratio of nickel to copper concentrations for particulates in the wet season. The internal cycling (adsorption/desorption) of dissolved nickel in both seasons was calculated as the difference in the dissolved flux out past the Dumbarton Bridge and the sum of all other dissolved fluxes into the Lower South Bay.

Other fluxes for the mass balance exercise (Tetra Tech, 1999) were obtained from various sources. Point source loads for Lower South Bay were calculated from average discharge flows reported by dischargers multiplied by average nickel concentrations. Atmospheric deposition rates were derived from preliminary results of the RMP atmospheric deposition pilot study (Tsai et al., 2001). Atmospheric loading rates calculated on completion of that study differ only slightly (~31 kg/y totaling wet and dry deposition), with atmospheric deposition still constituting a minor portion of overall loading. Tributary loads were modeled for Lower South Bay watersheds using concentrations from City of San Jose and flow data from a USGS gauge station (URS Greiner Woodward Clyde, 1998). Diffusive flux was estimated assuming a gradient from negligible nickel at the sediment water interface, up to the bulk porewater concentration within the top 1 cm of the sediment surface.

The estimated flux of total nickel exiting the Lower South Bay was approximately 15,000–17,000 kg in the dry season (Table 3) and 12,000–14,000 in the wet season. Dry season estimated dissolved nickel flux was 900–1700 kg. The greatest contribution of total nickel to the water column of Lower South Bay was particulate flux from the bed, followed by loading from wastewater treatment plants. As expected, the largest difference between the dry and wet seasons was the contribution of the tributaries.

Table 3
Total nickel mass balance calculations for Lower South San Francisco Bay (Region 5), from Tetra Tech (1999)

Ni influx into LSB	kg/dry season (% dissolved)	kg/wet season (% dissolved)
Atmosphere	15 (0%)	15 (0%)
Tributaries	40 (80%)	6000 (10%)
Wastewater treatment	800 (80%)	940 (80%)
Diffusion from sediments	360 (100%)	360 (100%)
Net particulate flux	16,000–18,000 (0%)	15,000–16,000 (0%)
Total flux into LSB	17,000–19,000 (5%)	22,000–23,000 (7%)
Fluxes out of LSB	15,000–17,000 (10%)	12,000–14,000 (7%)
Dissolved adsorption(–) desorption(+) to balance	+ 700	–600
Water column loss(–) or gain(+) needed to balance	–2700	–9400

Total nickel loadings from tributaries were predicted to be much higher in the wet season (~6000 kg) than in the dry season (~40 kg). However, for both seasons, the largest predicted fluxes into Lower South Bay water column were from the net resuspension of bedded sediments, estimated from a mass balance of nickel within the segment, assuming a steady state (total in = total out) for particulate nickel in the water column of Lower South Bay (Table 3).

The diffusive flux of nickel from the sediment to the water column (720 kg/y) agrees with estimates based on empirical measurements of benthic flux of dissolved nickel in the South Bay (Region 4) made by Topping and Kuwabara (2003), but diffusive fluxes and atmospheric deposition are much smaller than the tributary and resuspension sources. Also, POTW loading has decreased dramatically over the past two decades. Ten years ago the loading from wastewater treatment plants was estimated to be 5400 kg/y, and the loading 20 years ago was estimated to be 12,000 kg/y (Tetra Tech, 1999).

Although the dry season net nickel fluxes into and out of the Lower South Bay water column balance reasonably well (the methodology balances exactly only for copper), the same is not true for the wet season. While influx and efflux are not required to match on a seasonal basis, wet season tributary flux may be overestimated due to uncertainties in various mass balance model parameters. Particulate nickel net flux from bedded sediment may also be overestimated, as the minimum estimated net nickel flux from this pathway alone supplies more than the maximum flux out of Lower South Bay in the wet season. However, whether these model discrepancies are accounted for through increased efflux out of Lower South Bay or decreases in net particulate flux from sediment (e.g. more sedimentation in wet season) or other sources, nickel resuspended from sediment likely is one of the two largest sources to the water column.

The mass balance of nickel described above was possible due to several unique circumstances in Region 5 of the Bay. The semi-enclosed nature of the Lower South Bay helped to constrain the fluxes of nickel at the southern part of the Lower South Bay, where they could be estimated based on available data. Prior hydrodynamic modeling work has been completed in this part of the Bay (Gross, 1997), allowing more accurate residence time estimates for calculating nickel fluxes at the Dumbarton Bridge (the boundary between South and Lower South Bay, Fig. 1) than would be possible between any other segments. Extensive data sets were available for both source and *in situ* concentrations that helped to constrain uncertainties. It would be difficult to develop, without significant effort, nickel mass balances in the northern and central reaches of the Bay, due in part to the hydrodynamic complexity in those regions.

However, even with only crude estimates for nickel inputs to the rest of the estuary, sediment inputs of suspended particulates are likely to dominate as well.

Rivera-Duarte and Flegal (1997) also identified sediment resuspension as the primary source (77%) of loading to San Pablo Bay. Assuming rates of diffusion and particle resuspension similar to Lower South Bay, scaling on the basis of area for the entire bay (~30 × that of Lower South Bay alone) would result in 21,600 kg/y diffusive flux of nickel, with 975,000 kg/y input of resuspended particulate nickel flux. The next largest flux of nickel is likely to be inflow from the Sacramento/San Joaquin Delta. Flows vary widely from year to year, but on average approximately 20% of flow occurs in the dry season (McKee et al., 2006). Total nickel concentrations at the RMP Sacramento and San Joaquin stations averaged 3.5 µg/L (60 nM, with 28% dissolved) in the dry season and 5.1 µg/L (87 nM, with 29% dissolved) in the wet season, so the Delta percentage contribution of dissolved nickel is fairly constant between seasons. Average loads of nickel from the Delta were estimated at 410,000 kg/y by Davis et al. (2000). Other loads included an estimated 49,000 kg/y from tributaries, 4800 kg/y in effluent, and 580 kg/y via atmospheric deposition. The loads estimated via these other pathways are of similar relative percentages as those for Lower South Bay alone, and roughly proportional to relative watershed drainage and bay water surface areas (~4 × and 30 × the respective areas for Lower South Bay) for tributary and atmospheric deposition estimates, and proportional to relative flows (~3 × Lower South Bay dischargers alone) for effluent.

2.3. Nickel cycling

Chemical speciation of nickel in water is important because it plays a major role in both the fate and toxicity of nickel that enters the Estuary. Accumulation rates and toxicity vary with the chemical forms of trace metals because of differences in bioavailability for uptake among chemical species (Sunda and Huntsman, 1998). Chemical speciation also influences abiotic fate and transport processes, affecting mobility and partitioning through complexation with dissolved organic ligands and adsorption to particulate organic or mineral phases. Sediments represent a substantial portion of the pool of nickel within the estuary, so cycling between the water and sediments is very important to its transport and fate in the ecosystem. Nickel cycling has been studied in San Francisco Bay by numerous researchers, including Luoma and Phillips (1988), Flegal et al. (1991), Donat et al. (1994), Sañudo-Wilhelmy et al. (1996), Rivera-Duarte and Flegal (1997), Luoma et al. (1998), Bedsworth and Sedlak (1999), Gee and Bruland (2002), and Flegal et al. (2005).

Nickel that enters the estuary through non-point source discharges is largely either associated with particulate material or complexed in dissolved species. Sedlak et al. (1997) found that dissolved (<0.45 µm) nickel accounted for approximately 45% of the total nickel in surface runoff samples. Colloidal species are not thought to be important in the extreme reaches of the Bay (Sanudo-Wilhelmy et al.,

1996). The primary particulate forms of nickel in non-point sources originate as metal ions adsorbed to upland sediments that erode and are transported in stream channels to the estuary or embedded in the matrix of soil particles at natural background levels. Dissolved nickel species from non-point sources consist of complexes with biogenic ligands in natural organic matter. Sedlak et al. (1997) found that 25% of the dissolved nickel in surface runoff samples was strongly complexed.

Similarly, nickel from point sources is also primarily in particulate form or as dissolved metal complexes. However, unlike diffuse non-point sources for which particulate fluxes currently are minimally (or not) controlled, wastewater treatment plants generally reduce particulate discharges through process controls such as flocculation, settling, and filtration. For example, dissolved nickel accounted for as much as 75% of the nickel in the wastewater effluents (Sedlak et al., 1997), versus ambient dissolved concentrations in Lower South Bay waters for wet and dry seasons of 25% and 60%, respectively, likely in part due to solids removal in wastewater treatment. Another factor contributing to dissolved nickel in municipal wastewater effluent is the presence of moderately strong complexes (i.e., metal complexes with humic material) and strong complexes of metal species stabilizing metals in the aqueous phase. The majority of the latter occurs as nickel ethylene diaminetetracetate (NiEDTA^{2-}) complexes, which has been identified as one of the major stable nickel species in wastewater effluents (Bedsworth and Sedlak, 1999).

As a result of the combination of sources of biogenic and anthropogenic ligands as well as nickel, much of the dissolved nickel in ambient samples from South San Francisco Bay is also strongly complexed (Bedsworth and Sedlak, 1999; Sedlak et al., 1997; Donat et al., 1994). In microcosm experiments, Beck et al. (2002b) found low bioavailability of nickel in the South Bay (Region 4) due to complexation by organic ligands, although Luoma et al. (1998) found approximately 25% depletion of surface water dissolved nickel concentration in a spring phytoplankton bloom, suggesting a remaining bioavailable dissolved nickel fraction in ambient waters under some circumstances. A summary of research conducted on dissolved nickel complexation in this area is presented in Table 4.

Because strongly complexed dissolved nickel from wastewater effluent and non-point sources would largely behave conservatively within the Bay, a significant portion of the aqueous nickel would not be readily bioavailable. This nickel could be transported from discharge points into the Central Bay, or even into the Pacific Ocean, before significant dissociation occurs. Furthermore, if these stable complexes constitute a larger fraction of wastewater effluents than in non-point sources, then equal reductions in concentrations and loadings from these differing source types would not result in equal decreases in bioavailable nickel.

For labile and moderately strong nickel complexes, their chemical speciation may change within the estuary as a result of changes in parameters such as pH, dissolved organic carbon concentrations, oxidation–reduction potential, salinity, affinity of metals for particulates (especially particulates that contain amorphous iron), and biologically mediated processes. The speciation of labile and moderately strong nickel complexes can in some cases be approximated as equilibrium processes, particularly when residence times are long relative to reaction rates.

The major inorganic ligands prevalent in water entering the estuary from the Pacific Ocean include chloride, sulfate, and (bi)carbonate (Brewer, 1975). The concentrations of these ligands will change with the seasons in different sections of the estuary, reflecting differences in water flows from various sources. Salinities in the sloughs and Sacramento–San Joaquin Delta can be as low as several psu, and salinities in the Bay can vary from about 10 to 15 psu to near sea water (~34 psu). However, these generally form weak complexes with nickel, with the dominant inorganic species, or half the dissolved nickel not organically complexed, existing as free nickel ions (Byrne, 2002; Donat et al., 1994), and other inorganic species accounting for the remainder. As a result, inorganic complexation may only slightly influence the bioavailability and uptake of any nickel not already organically complexed.

The combined RMP and City of San Jose data set were used to examine the partitioning of nickel between the solid and dissolved phases and to investigate the relationship between these monitoring data and the various measurements of nickel speciation (e.g., Sedlak et al., 1997; Donat et al., 1994; Bedsworth and Sedlak, 1999; Gee and Bruland, 2002). Mean distribution coefficients (K_D) were calculated by region of the Bay from the ratios of nickel concentrations in suspended particulates to those in the dissolved phase. Values of $\log K_D$ for the regions are presented in Table 5 for both the wet and dry seasons.

Table 4
Estimated dissolved nickel complexes in various source and ambient waters of San Francisco Bay

Reference, matrix	% Strong	% Moderate	% Weak
Sedlak et al., 1997, wastewater	75%	15%	10%
Sedlak et al., 1997, runoff	25%	15–45%	25%
Bedsworth and Sedlak, 1999, wastewater	55–70%	15%	20%
Bedsworth and Sedlak, 1999, ambient (moderate + weak)	0–90%	10–100%	
Donat et al., 1994, ambient	35–50%		50–65%
Beck et al., 2002b, ambient			<25%
Luoma et al., 1998, ambient	75%		25%
Ndung'u et al., 2003, ambient	>10–20%		

Table 5
Values of the distribution coefficient ($\log K_D$) between dissolved and particulate nickel concentrations in San Francisco Bay

Region	Wet	Dry
1 (Suisun)	4.84	4.90
2 (San Pablo)	4.66	4.78
3 (Central)	4.95	5.00
4 (South)	4.69	4.62
5 (Lower South)	4.46	4.33

In both seasons, the lowest mean K_D values were calculated for Region 5 (Lower South Bay) and the highest for Central Bay (Region 3). Mean K_D values differed between Regions 5 and 3 by a factor of three or greater, and K_D for these two regions were, respectively, significantly lower and higher than Regions 1, 2, and 4.

The observed gradient in the K_D values between the Lower South Bay (Region 5) and the Central Bay (Region 3) is consistent with the findings that a large portion of the nickel loading in the Lower South Bay is from wastewater treatment plants (Flegal and Sanudo-Wilhelmy, 1993) and that the dissolved nickel from this source is largely bound by inert organic ligands (Bedsworth and Sedlak, 1999) and thus more likely to remain dissolved. The increase in K_D values from Lower South Bay (Region 5) to South Bay (Region 4) may be due to decreasing contributions of nickel and complexing organic ligands from wastewater relative to input of less-strongly complexed dissolved nickel from sediments (Topping and Kuwabara, 2003). The higher K_D values in the Central Bay continue this spatial trend in decreased importance of organic ligands in controlling the adsorption kinetics. K_D values for nickel from the northern reach of the Bay (Region 1) were more similar to those observed in the Central Bay and also may reflect a decreased role of organic complexes in nickel speciation and adsorption, as average dissolved organic carbon is usually lowest in Regions 1 and 3 (averaging 1700 and 2300 $\mu\text{g/L}$ in RMP data) and highest in Region 5 (averaging 3200 $\mu\text{g/L}$).

3. Sediment

The RMP has collected surface sediment samples (0–5 cm depth composites) from 1993 through the present. Prior to 2002, sediment samples were collected annually at 26 fixed sites; in 2002, a randomized sampling design was implemented at to provide a more representative picture of sediment concentrations. Approximately 47 random sites are now sampled each year. At the time the program moved to a randomized sampling design, the program also switched from analyzing sediment in both the wet season (February/March) and dry season (July/August) to analyzing once per year in the dry season. This paper focuses on RMP data collected between 1993 and 2003 and places them in historical context with data collected by the USGS

Bay Program. More information regarding the sample collection and handling, data validation, and quality assurance/quality control protocols can be found in the Annual Monitoring Results for each year and in the 1999 Quality Assurance Program Plan available from the SFEI website (http://www.sfei.org/rmp/rmp_docs.html).

Nickel concentrations in San Francisco Bay were generally higher than concentrations observed in sediments from other estuaries and oceans (Fig. 3). Concentrations of nickel in San Francisco Estuary sediments averaged (\pm standard deviation (st. dev.)) 85.9 (± 24.1) $\mu\text{g/g}$. This average concentration is much higher than concentrations observed in regional surveys of coastal areas of Southern California (Noblet et al., 2003, Katz and Kaplan, 1981), estuaries in the United Kingdom (Bryan and Langston, 1992), and Baffin Bay in Canada (Campbell and Loring, 1980) (Fig. 3). In fact, concentrations of nickel in San Francisco Bay sediments were among the highest of any estuary in the United States. In a survey of results from coastal and estuarine sediment monitoring programs across the United States, Daskalakis and Connor (1995) noted that only 0.1% of 13,433 samples collected from 3878 sites surveyed had nickel sediment concentrations above 42 $\mu\text{g/g}$.

The range of concentrations observed by the RMP in sediment is consistent with other observations reported for the San Francisco Estuary. Hornberger et al. (1999) advanced six cores to a depth of approximately 2 m; three cores located in San Pablo Bay, Central Bay, and Richardson Bay were analyzed for nickel. Mean concentrations (\pm st. dev.) in these cores were: 73.3 \pm 4.1, 85.3 \pm 7.6, and 103 \pm 15 $\mu\text{g/g}$, respectively. Concentrations of nickel in core sections did not vary significantly with depth, in marked contrast to other contaminants such as mercury that have had substantial historical anthropogenic inputs.

The RMP surface sediment data correlates well with the US Environmental Protection Agency's Environmental Monitoring and Assessment Program (EMAP) data. EMAP collected surficial sediment samples at random sites in the estuary from 2000 to 2001 (EMAP, 2000–2001). Agreement of the RMP data from 1993 to 2003 with the EMAP data is quite good; the mean nickel value for EMAP data was 93.0 \pm 17.4 $\mu\text{g/g}$ versus a mean value for RMP data of 85.9 \pm 24.1 $\mu\text{g/g}$. Fig. 4 shows a plot of nickel concentrations in shallow sediments using both RMP and EMAP data.

It is likely that the high concentrations of nickel observed in Bay sediments are largely a result of the geologic composition of the surrounding watershed rather than anthropogenic emissions (Hornberger et al., 1999; Topping and Kuwabara, 2003). The Coastal Range that surrounds the San Francisco Estuary and Tomales Bay is enriched with nickel-bearing formations such as the Franciscan Complex (Oze et al., 2004). This formation is composed of significant amounts of greywacke, shale, serpentinite, and partially serpentized ultramafic (high in

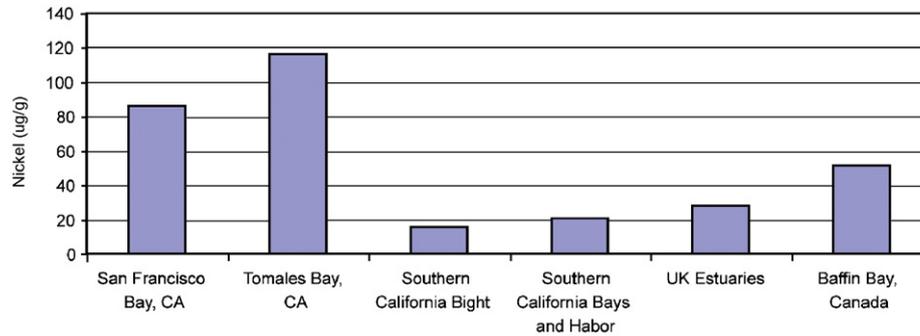


Fig. 3. Average concentrations of nickel observed in estuaries and bays (Source: RMP data, Noblet et al., 2003; Katz and Kaplan, 1981; Bryan and Langston, 1992; Campbell and Loring, 1980).

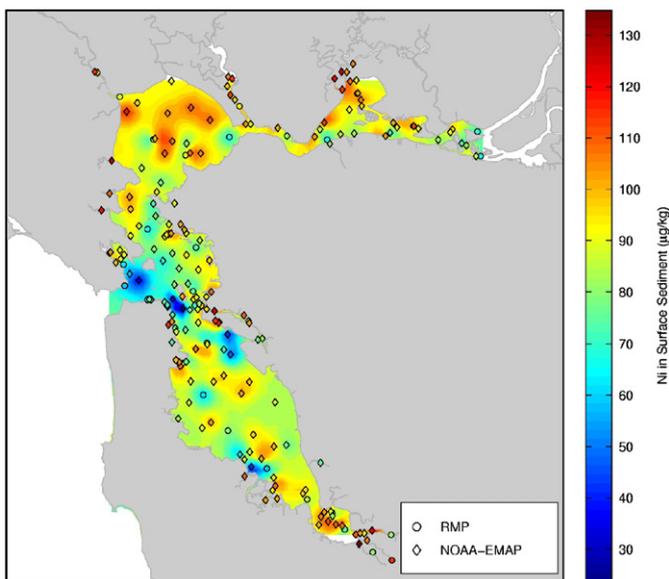


Fig. 4. Nickel concentrations in surface sediments of San Francisco estuary. (Source: RMP data 1993–2003 and EMAP, 2000 and 2001).

other (less than 45 km apart) and contain many of the same geologic formations in sediments eroded from their respective watersheds.

3.1. Spatial trends

A statistical evaluation of the RMP data using the Tukey–Kramer means comparison ($p \leq 0.05$) indicates that the segments fall into three distinct groups: the tributaries to the Lower South Bay (highest mean concentration, $125.6 \mu\text{g/g}$), the Lower South Bay and Suisun and San Pablo Bays (range of means from $88.6 \mu\text{g/g}$ to 101.6), and the San Joaquin/Sacramento rivers and Central and South Bays (means ranging from 75.5 to $76.8 \mu\text{g/g}$).

The spatial variation of nickel in the sediment of the estuary, with lower concentrations in the Central Bay as compared to the North and South Bays (Fig. 4), parallels the distribution of nickel in water as discussed above. Sediments in Suisun Bay, San Pablo Bay, and Lower South Bay and tributaries of Lower South Bay had higher concentrations of nickel than other segments, which is likely attributable to wastewater treatment plants and stormwater runoff from the surrounding watersheds which are high in nickel (Davis et al., 2000; Hornberger et al., 1999). Higher nickel concentrations were observed in the areas that receive substantial drainage from the Coastal Range (e.g., Suisun, San Pablo, and Lower South Bay) combined with anthropogenic inputs, with lower nickel concentrations found in areas nearer sediment sources with lower nickel concentrations such as the Pacific Ocean ($\sim 40 \mu\text{g/g}$ Bodega Bay, Meador et al., 1994) or the Sacramento/San Joaquin Delta ($77 \mu\text{g/g}$ average for RMP data) (Fig. 5).

3.2. Temporal Trends

In general, there appears to be no overall increasing or decreasing trend for nickel in the estuary, although some significant interannual variation has been observed. A statistically significant difference in means was noted for 1998 (Student t test, $p \leq 0.05$). Record rainfall events occurred in the winter of 1997/1998, which was ranked as

iron and manganese) igneous rocks (Blake et al., 2000). Nickel concentrations in serpentine and ultramafic rocks from the San Francisco Bay area ranging from 1000 to 3300 mg/kg have been reported (Parker, 1967; Bailey and Everhart, 1964; Oze et al., 2004). Himmelberg and Coleman (1968) reported similar ranges of concentrations for the serpentinized ultramafic rocks in the Coastal mountains to the east of the South Bay.

The similarity of concentrations observed in San Francisco estuary sediments to those in Tomales Bay sediments (Fig. 3) corroborate the hypothesis that the primary source of nickel in sediments is a result of the geology of the area, not anthropogenic sources. With the exception of a former mercury mine, Tomales Bay is notably devoid of anthropogenic trace metal sources. This is in marked contrast to the San Francisco estuary that has numerous municipal and industrial sources (Monroe and Kelly, 1992; Flegal et al., 2005; Hornberger et al., 1999). The two areas, however, are in close proximity to each

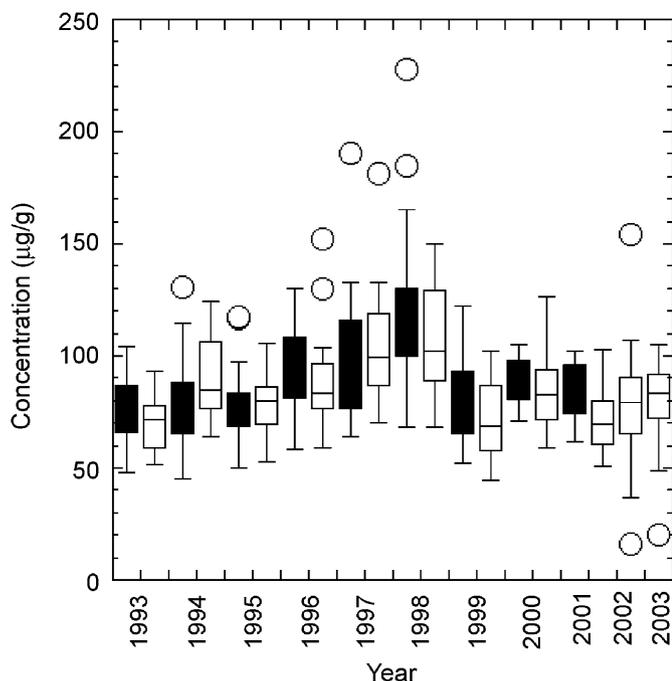


Fig. 5. Nickel concentrations in RMP sediment over time. Darkly colored boxes indicate wet weather sampling which ceased in 2001. Circles indicate statistical outliers. (Sediment sampling events 1993 through 2001 occurred biannually at fixed sites. In 2002, the program switched to random sites sampled only in the dry season (July/August).)

one of the top 10 wettest winters of the century (NOAA, 1998), although sediment loads and nickel concentrations were not directly measured for tributaries in surrounding watersheds during that period. Work conducted by Davis et al. (2000) suggests that significant mass loading occurs from tributaries into the estuary. Based on historical suspended sediment data from monitoring stations on the Sacramento River and measurements of Delta outflow, it was estimated that approximately 410,000 kg of nickel per year (kg/y) are transported into the estuary, but much of that material would contain lower concentrations of nickel as typically seen at the Sacramento and San Joaquin River sites for the RMP.

Similar estimates were made for other sources and were found to be significantly lower (e.g., urban tributaries contributed approximately 49,000 kg/y; municipal effluent was an order of magnitude lower at 5200 kg/y), although data in that analysis for extreme runoff events such as those in 1998 were sparse for the urban tributaries. In general, with the advent of tertiary treatment and an increasing regulatory focus on trace elements (e.g. pre-treatment requirements under the Clean Water Act that were implemented in the early 1970s as well as the Toxic Release Inventory reporting requirements that were implemented in 1986), significant decreases in metal loadings from POTWs have occurred since the 1960s (Monroe and Kelly, 1992; Flegal and Sanudo-Wilhelmy, 1993; Squire et al., 2002). In addition, the average daily flow from POTWs into the Bay has decreased dramatically from 855 million

gallons per day (MGD) in the mid-1980s (Monroe and Kelly, 1992) to approximately 600 MGD in 2000 (SFEI, 2006). Squire et al. (2002) estimated that total trace metal loadings (e.g., As, Cd, Cr, Cu, Pb, Hg, Ni, Se, Ag, and Zn) to the Bay from POTWs has been reduced approximately 20-fold (e.g., 993 t per year in 1960 to 46 t per year in 1999). It is likely that storm events such as those that occurred in 1998 are among the largest nickel loads to the estuary. A similar review of sediment data specifically for the southern San Francisco Estuary from 1990 to 1998 and select years in the 1970s and 1980s (Hornberger et al., 2000) did not identify any temporal trends for nickel.

3.3. Sediment processes

The concentration ranges of nickel observed in surface sediments are consistent with our understanding of the geology of the surrounding watersheds and hydraulic processes. The concentrations of nickel in sediment are influenced by resuspension and adsorption/desorption kinetics (Topping and Kuwabara, 2003; Gee and Bruland, 2002; Martino et al., 2004).

The shallow bathymetry of the estuary, tidal flows, and strong winds result in sediment being resuspended into the water column and redistributed within the embayments. The average depth of the estuary is 6 m, and some embayments, such as San Pablo, are very shallow, averaging 2 m (Conomos, 1979). In contrast to other contaminants such as polychlorinated biphenyls (PCBs), concentrations of nickel are relatively uniform within each of the embayments. This is likely largely a function of a numerous non-point sources of nickel in sediments from surrounding watersheds and the remixing of sediments as a result of estuarine processes. Evidence of this disperse geologic source is seen in analyses of deep bay sediment cores analyzed by Hornberger et al. (1999); nickel in core sections did not vary significantly with depth, in marked contrast to other contaminants such as mercury that have had substantial historical anthropogenic inputs.

In addition to resuspension of sediment, nickel concentrations in sediment are also influenced by adsorption/desorption kinetics. Research by Topping and Kuwabara (2003) indicated that net nickel flux from the South San Francisco Bay sediments was almost always positive (out of the sediment). The estimated flux of nickel from the sediment to the water column was 29 kg/day, greater than the flux from wastewater treatment of 3 kg/day, suggesting that sediments may be a significant source of nickel to the water column. Similar work by Gee and Bruland (2002) suggests that the sediment adsorption/desorption kinetics of nickel are slow in comparison to other metals such as copper and zinc; nonetheless, the sediments remain a significant source of nickel to the Bay. Using isotopes to understand the equilibrium partitioning in San Francisco Bay, Gee and Bruland (2002) estimated that in the absence of perturbations, the system will come into equilibrium in one month.

4. Biological effects

4.1. Biological cycling and food web accumulation

Aquatic organisms influence the biogeochemical cycling of nickel and other trace metals through uptake and excretion processes, incorporation into biological tissues, and production of metal-containing organic detritus. Uptake removes dissolved metals from the water column and incorporates them in the biota, while excretion and remineralization returns metals back to the water in soluble forms. However, this biological processing can change the form and bioavailability of the metals. Free metal ions and weak complexes with inorganic species are the forms that are most readily assimilated from the water, while excreted forms may be complexed with organic ligands that are much less available for uptake (Sunda and Huntsman, 1998).

Uptake removal fluxes of nickel from the water depend on the product of the uptake rates, bioavailable metal concentrations in the water, and organism densities. Excretion fluxes are a function of the excretion rates, metal concentrations in the organisms, and organism densities. Because microbial organisms and phytoplankton typically have higher uptake and excretion rates than biota at higher trophic levels (due to their high surface-to-volume ratios and high metabolic activities, as well as a higher total biomass typical for lower trophic levels in food webs), they are a larger component of the biogeochemical cycling of trace metals in San Francisco Bay.

4.2. Phytoplankton

Phytoplankton uptake and regeneration are known to play an important role in nickel and other trace metal cycling in the oceans, and are thought to control the vertical concentration profiles of these metals in the upper portion of the water column in the open ocean (Bruland et al., 1991; Sunda and Huntsman, 1995). The importance of phytoplankton uptake in estuaries is less clear. However, dissolved nickel removal, as well as reduction of other metals such as zinc and cadmium, was detected during a bloom in South San Francisco Bay (Luoma et al., 1998): at the height of the spring phytoplankton bloom, dissolved nickel concentrations were reduced to 75% of the pre-bloom concentrations. These results suggest that phytoplankton uptake of metals could be an important process affecting nickel concentration and cycling and serve as a pathway for transfer of nickel to higher trophic organisms or to the sediment after death and settling of the bloom.

Nickel in laboratory phytoplankton (diatom) cultures grown in water from the South Bay near the Dumbarton Bridge with 40 nM dissolved nickel approached 100 a mol/cell (Phinney and Bruland, 1997). Assuming similar uptake in the field, cell densities of approximately 10^8 cells/L would deplete dissolved nickel by 25% (10 nM) seen by Luoma et al. (1998), although phytoplankton cell densities

were not measured in that work. Cloern (1979) reviewed previous work on phytoplankton dynamics in San Francisco Bay, with typical San Francisco Bay phytoplankton bloom densities ranging 10^5 to 10^7 cells/L. Tadros et al. (1990) found growth inhibition up to ~50% in synthetic seawater cultures for some species of diatoms from the Gulf of Mexico at concentrations of 10 nM nickel, although several other species showed no inhibition at that concentration.

4.3. Fish

There have been limited measurements of nickel in fish from San Francisco estuary, although Starry flounder (*Platichthys stellatus*) from San Pablo and Central Bay (Hunters Point), and White croaker (*Genyonemus lineatus*) from Central (Hunters Point, Oakland, Islais Creek) and South Bay (Redwood City) were collected in the NOAA National Benthic Surveillance Project (Meador et al., 1994) prior to the start of RMP (1984–1988). Fish tissue nickel concentrations in that study averaged below 1 µg/g dry weight, far below the MTRL for nickel in edible tissues from enclosed bays and estuaries of 220 µg/g wet weight (Rasmussen, 1994), which given typical moisture content seen in fish from the estuary of 70–80% (SFEI, 1999) would translate to dry weight MTRLs of 700–1100 µg/g.

4.4. Bivalves

Bivalves (*Mercenaria*, *Crassostrea*) are among the most sensitive species used in the derivation of the EPA aquatic life water quality criteria (USEPA, 1976, 1986). Although the species are not identical to those used in criteria development, the RMP uses transplanted bivalves as one of the tool to monitor the uptake of contaminants into the food web. In addition, transplanted bivalves can be an excellent trend indicator for organic contaminants and some trace elements such as copper and silver (see Davis et al., this issue for a discussion of PCBs in bivalves; Hornberger et al., 2000; Brown et al., 2004). Over the 10-year period, three different species of transplanted bivalves have been used: *Mytilus californianus*, *Corbicula fluminea*, and *Crassostrea gigas*.

Nickel can be toxic to biota at elevated concentrations because it competes with other physiologically important ions such as calcium and magnesium, and it can substitute in metalloproteins, causing disruption in cellular functions (Pane et al., 2003, Tetra Tech, 1999). A review of the RMP nickel data for the 10-year period indicates the average concentration observed in bivalves was highly variable, ranging 0.905–113.0 µg/g dry weight, although the upper limit is an outlier, most likely due to sediment contamination of the tissue analyzed. Typical concentrations average around 10 µg/g or lower. Even including the potential outlier, the range is substantially below the concentrations at which reduced survival rates are reported (328.4 to 1456 µg/g in Jarvinen and Ankley, 1999), suggesting that

there is little potential for biological impact. These tissue concentrations were also well below the nickel MTRL for enclosed bays and estuaries (Rasmussen, 1994), which adjusted for average moisture content (~85%) in RMP bivalve data would be ~1500 µg/g dry weight.

No temporal trends were identified over the ten-year period, which is consistent with the relatively constant sediment concentrations described above. In a review of nine years of National Mussel Watch data, Beliaeff et al. (1997) also noted no significant trend in the nickel bivalve data. Similarly Lauenstein and Daskalakis (1998) reviewed four large scale monitoring programs (i.e., US EPA monitoring data (1965–1972), EPA Mussel Watch Program (1976–1978), the National Oceanic and Atmospheric Administration's Mussel Watch Project (1986–1998), and the California Mussel Watch Program (1977–1998), and the authors also did not observe a significant trend in nickel data.

The highest value detected was in a bivalve sample from Suisun Bay (113 µg/g); however, this value is greater than four times the standard deviation and therefore, is considered a statistical outlier and excluded from the data set for analysis of segments. A comparison of means indicates that South Bay (10.8 µg/g) was significantly different ($p \leq 0.05$) from San Pablo Bay (6.6 µg/g), using a Student *t*-test means comparison. All other segments were not statistically different.

5. Conclusions

In the early 1990s, nickel concentrations in water in South San Francisco Bay frequently exceeded water quality objectives. In-depth studies that followed the listing of the South San Francisco Bay as an impaired water body indicated that dramatic declines in nickel loadings from wastewater treatment plants had occurred between the early 1980s and mid-1990s. Another substantial loading to the Bay is from nickel-bearing rocks in the local watersheds. Although wastewater treatment plant loadings have decreased dramatically over the years, as a result of the shallow bathymetry of the bay, much of the historical loadings to sediment are likely resuspended and recycled into the water column. Nickel speciation studies suggest that much of the nickel present in the water column is not in a form that is readily bioavailable. In light of this information, the California State Water Resources Control Board approved revised site-specific water quality objectives (SSOs) for the Lower South Bay in 2002. The technical justification for these SSOs (CEP, 2005b) renders them applicable bay-wide. The adoption of these nickel SSOs throughout San Francisco Bay have been recommended by the Clean Estuary Partnership copper/nickel workgroup. The results of long-term monitoring of nickel in the Bay have assisted in understanding the fate and distribution of nickel in the Bay and helped to develop new water quality objectives that are protective.

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