The effects of the San Francisco Bay plume on trace metal and nutrient distributions in the Gulf of the Farallones

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Abstract

The distributions of particulate elements (Al, P, Mn, Fe, Co, Cu, Zn, Cd, and Pb), dissolved trace metals (Mn, Fe, Co, Cu, Zn, and Cd), and dissolved nutrients (nitrate, phosphate, and silicic acid) were investigated in the Gulf of the Farallones, a region of high productivity that is driven by the dynamic mixing of the San Francisco Bay plume, upwelled waters, and California coastal surface waters. Particulate metals were separated into >10 and 0.4–10 μm size-fractions and further fractionated into leachable (operationally defined with a 25% acetic acid leach) and refractory particulate concentrations. Dissolved metals (< 0.4 μm pore-size filtrate) were separated into colloidal (0.03–0.4 μm) and soluble (<0.03 μm) fractions. The percent leachable particulate fractions ranged from 2% to 99% of the total particulate concentration for these metals with Mn and Cd being predominantly leachable and Fe and Al being predominantly refractory. The leachable particulate Pb concentration was associated primarily with suspended sediments from San Francisco Bay and was a tracer of the plume in coastal waters. The particulate trace metal data suggest that the leachable fraction was an available source of trace metal micronutrients to the primary productivity in coastal waters. The dissolved trace metals in the San Francisco Bay plume and freshly upwelled surface waters were similar in concentration, with the exception of Cu and Co, which exhibited relatively high concentrations in plume waters and served as tracers of this water mass. The dissolved data and estimates of the plume dynamics suggest that the impact of anthropogenic inputs of nutrients and trace metals in the San Francisco Bay plume contributes substantially to the concentrations found in the Gulf of the Farallones (10–50% of estimated upwelled flux values), but does not greatly disrupt the natural stoichiometric balance of trace metal and nutrient elements within coastal waters given the similarity in concentrations to sources in upwelled water. In all, the data from this study demonstrate that the flux of dissolved nutrients and bioactive trace metals from the San Francisco Bay plume contribute to the high and relatively constant phytoplankton biomass observed in the Gulf of the Farallones.
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1. INTRODUCTION

The Gulf of the Farallones, located just west of San Francisco Bay in the eastern boundary of the North Pacific, is a highly productive shelf region of the coastal waters off California (Fig. 1). The nutrient dynamics of these waters are similar to the rest of the California coast, and are dependent upon upwelling events that deliver macronutri-ents and trace metal micronutrients from the subsurface waters into the euphotic zone (Hutchins et al., 1998; Bruland et al., 2001; Fitzwater et al., 2003). However, the Gulf of the Farallones has an additional source of nutrients and trace metals that are supplied to its surface waters by the San Francisco Bay plume (Flegal et al., 1991; van Geen and Luoma, 1993).

The formation of the San Francisco Bay plume is due to coastal seawater that has entered the Bay on flood tides and has mixed with existing San Francisco Bay water and incoming freshwater from the Sacramento and San Joaquin Rivers, whereby the water becomes altered prior to return-

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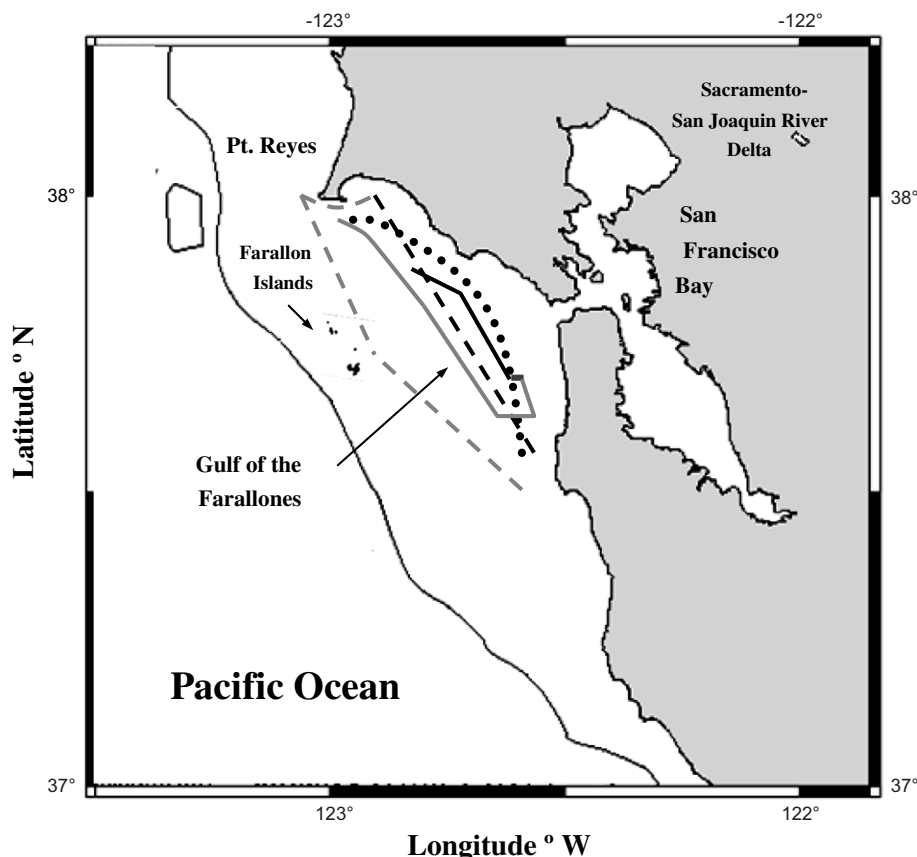 *E-mail address:* mph3@humboldt.edu (M.P. Hurst).

Fig. 1. Site map indicating surface transects along the continental shelf in the Gulf of the Farallones during July 1999 (━ ━), February 2003 (●●●●), and June 2004 (━━━). The July 1999 and June 2004 transect data are divided into two segments, Transect A (black) and Transect B (gray).

ing as the San Francisco Bay plume on the ebb tide. The supply of coastal seawater into the Bay far exceeds the average river input, resulting in a San Francisco Bay plume that has a relatively high salinity (Conomos, 1979). Once in the coastal waters, the plume is directed by the prevailing winds and surface water currents north, west, or south over the relatively broad continental shelf of the Gulf of the Farallones (Lentz, 1987; van Geen and Luoma, 1993). The chemical constituents of the plume differ from the river and coastal seawater entering San Francisco Bay because the saline estuary has its own internal cycling of nutrients and trace metals that is largely driven by anthropogenic inputs within the estuary (Flegal et al., 1991; Cloern, 1996).

The present investigation was pursued to assess the importance of the San Francisco Bay plume as an active and continual source of nutrients and trace metals to the Gulf of the Farallones, potentially enhancing the productivity in this region. The study encompasses both summer and winter conditions and can be used to further our understanding of the effects of the plume on coastal waters. A previous study (van Geen and Luoma, 1993) of some contaminant dissolved trace metals in the Gulf of the Farallones area reported an enrichment of Cd, Cu, Ni, and Zn originating from San Francisco Bay, with the property-salinity plots indicating an internal source within the Bay during the summer period. The extrapolation of the data

within these plots to zero salinity resulted in an interpretation that suggested elevated internal sources of trace metals existed within the San Francisco Bay estuary, values higher than the contaminant trace metal fluxes estimated by Flegal et al. (1991). The zero salinity estimates by Flegal et al. (1991) were produced by data solely collected inside the estuary. Shiller (1996) later used a simple box model to conclude that this discrepancy between these two zero salinity estimates was due to the trace metal flux from upwelled water within the Gulf of the Farallones. The limited study by van Geen and Luoma (1993) acknowledged the importance of upwelling as an end member but did not account for its trace metal contributions to surface waters. There is a need to better understand the individual contributions of the various end members within the Gulf of the Farallones and the seasonal variability of micronutrient and contaminant trace metal distributions. In addition, the importance of soluble vs. colloidal trace metals within the dissolved fraction and of chemically-labile particulate trace metals in the surface shelf waters needs to be included in the overall evaluation of biologically available nutrient and contaminant sources.

There are multiple sources that contribute to the levels of nutrients and trace metals in the San Francisco Bay plume and adjacent coastal waters. The trace metals within the San Francisco Bay estuary have been characterized in

previous studies [e.g., dissolved (Flegal et al., 1991), colloidal (Sañudo-Wilhelmy et al., 1996), particulate/dissolved (Gee and Bruland, 2002), porewaters (Rivera-Duarte and Flegal, 1994; Spinelli et al., 2002), sediments (Hornberger et al., 1999), and dissolved speciation (Donat et al., 1994; Hurst and Bruland, 2005)]. The presence of elevated trace metal concentrations in the estuary is largely due to present and historical anthropogenic activity in the watershed, which drains 40% of California's surface area and is surrounded by 7 million inhabitants in the San Francisco–San Jose–Oakland metropolitan area (van Geen and Luoma, 1999). Contaminant trace metals (Cu, Pb, Co, and Zn) associated with anthropogenic sources have major internal sources within San Francisco Bay (Flegal et al., 1991). Dissolved nutrients such as phosphate and nitrate have also been interpreted as having major internal sources in San Francisco Bay, namely wastewater treatment effluent and diagenetic fluxes from historically contaminated sediments (Flegal et al., 1991). The riverine input from the Sacramento–San Joaquin River delta at the farthest northern reaches of San Francisco Bay also delivers dissolved trace metals and nutrients, an abundance of silicic acid, and approximately 3×10^6 metric tons of suspended sediments annually (Griggs and Hein, 1980). A portion of this sediment load is distributed along the continental shelf in the Gulf of the Farallones and accumulates in the mudbelts along the continental shelf at depths of 50–100 m (Wheatcroft et al., 1997). The resuspension of these fluvial inputs during spring–summer–fall upwelling events has been reported to be an important mechanism for the transport of iron to the surface waters (Johnson et al., 1999; Bruland et al., 2001). It can be speculated that other trace metals associated with these sediments would also become resuspended. This resuspension process is strengthened along the shelf waters in the Gulf of the Farallones due to its position south of Point Reyes, for it is known that the most intense upwelling in this region occurs in localized areas south of protruding landmasses such as capes or points (Strub et al., 1991).

Lastly, an important aspect of the trace metal data to be presented is the determination of the leachable particulate fraction measured in the plume and the comparison of this fraction in both winter and summer. The suspended particulate matter in the plume contains both chemically labile and refractory materials. The labile trace element fraction, defined here as the fraction of an element that can be dissolved in a 2-h acetic acid leach (pH 2, room temperature), consists of particle coatings in association with amorphous oxyhydroxide precipitates, carbonate minerals, adsorbed species, and chelated species associated with particulate organic matter (Landing and Bruland, 1987). When these trace metals are transported to the surface waters during strong upwelling events or delivered by runoff, it has been suggested that a part of the labile particulate fraction may become redissolved and available for assimilation into phytoplankton growth cycles (Wells and Mayer, 1991; Wells et al., 2000; Bruland et al., 2001; Fitzwater et al., 2003; Buck et al., 2007). Because the fresh particles coated with chemically labile trace metals are deposited on the coastal shelf primarily during the highest river discharge

in the winter months, but are made available during spring–summer upwelling events (Johnson et al., 1999), it is of interest to measure and compare the chemically labile trace metal fraction in these two distinct seasonal patterns.

2. METHODS

2.1. Sample collection and handling

The collection of surface water samples and hydrographic data was performed on three research cruises in the California coastal waters in the summer of 1999 (July 3), winter of 2003 (February 14–15), and summer of 2004 (June 23) aboard the R/V Point Sur (Fig. 1). Samples were collected with a clean surface pump system that included an all PTFE Teflon™ diaphragm pump (Bruiser™, Osmonics) and PFA Teflon™ tubing (Bruland et al., 2005). The sample inlet was lowered to 1 to 2 m below the sea surface during transects and mounted to a PVC fish system, which was deployed off the ship's forward side beyond the influence of the wake. During transects, at speeds between 4 and 7 knots, temperature, salinity, percent transmittance, and fluorescence measurements were collected with an underway system.

All sample preparation and acid cleaning was conducted in a HEPA-filtered Class 100 laminar flow clean area (Hurst and Bruland, 2007). Unfiltered samples were collected in acid-cleaned, two-liter, low-density polyethylene (LDPE) (Nalgene) bottles and filtered sequentially through 10 and 0.4 μm pore size polycarbonate track-etched (PCTE) filters (47 mm dia., Nuclepore™, Whatman) mounted in consecutive polypropylene filter sandwiches (Millipore). A subset of the unfiltered samples during the June 2004 sampling event were also passed through a 0.03 μm polyethylene hollow fiber flow-through filter (700 cm², Sterapore™, Mitsubishi-Rayon) mounted in a polycarbonate capsule. These filters were cleaned and maintained as described by Nishioka et al. (2001a). The soluble fractions were operationally defined by this 0.03 μm nominal pore size; thus, the colloidal trace element concentrations were estimated by taking the difference between measured values in the 0.4 and 0.03 μm filtrates. Sample outlets were used for simultaneous collection of 0.4 and 0.03 μm filtrates from a two liter LDPE sample (~5 psi) with N_2. The filtrate samples were acidified to a pH of ~1.7 (equivalent to 4 mL of sub-boiled, quartz-distilled, 6 M HCl per liter of seawater). All acidified filtrate samples were stored for at least 3 months prior to being analyzed. Samples for dissolved nutrients were analyzed aboard ship in July 1999 and June 2004, while discrete samples were collected and frozen in February 2003 for analysis at a later date. The dissolved concentrations of nitrate, phosphate, and silicic acid were measured with a Lachat QuickChem 8000 Flow Injection Analysis system using standard methods (Parsons et al., 1984).

2.2. Particulate and dissolved trace metal analyses

The extraction of the leachable trace element fraction from the frozen PCTE filters was performed by delivering 2 mL of 25% quartz-distilled acetic acid (QHAc) into a

7 mL vial and allowing contact with the folded filter for 2 h at room temperature (Chester and Hughes, 1967). The leachate and rinses of the filter were removed, placed into an acid-cleaned quartz beaker and heated to dryness (Landing and Bruland, 1987). The resulting residue was redissolved in 1 M $QHNO_3$. Each filter and the associated refractory particulate material was then microwave-bomb digested with 2 mL of concentrated quartz-distilled nitric acid ($QHNO_3$) and 50 μL of concentrated trace metal grade HF in PTFE Teflon™ bombs (Savillex, Minnetonka, MN). The final digest solution was diluted to yield a 1 M HNO_3 matrix solution.

Analyte concentrations in particulate (Al, P, Mn, Fe, Co, Cu, Zn, Cd, and Pb) and dissolved trace metal (Mn, Fe, Co, Cu, Zn, and Cd) fractions were prepared and measured using a Thermo-Electron Element 1 magnetic sector HR-ICP-MS with a PFA Teflon™ spray chamber and PFA-ST nebulizer (Elemental Scientific) (Hurst and Bruland, 2007). The analysis of leachable and refractory particulate trace elements was performed by pumping solutions directly to the PFA nebulizer and data were acquired in low resolution (^{111}Cd, ^{206}Pb, ^{207}Pb, and ^{208}Pb) and medium resolution (^{27}Al, ^{31}P, ^{55}Mn, ^{56}Fe, ^{59}Co, ^{63}Cu, and ^{66}Zn) modes. The intensities of these analytes, relative to the internal standard, were quantified using the method of standard addition. It was necessary to correct the ^{111}Cd intensity for $^{95}Mo^{16}O$ interference, and Pb concentrations were determined by the summation of isotopes ^{206}Pb, ^{207}Pb, and ^{208}Pb. Dissolved trace metal analyses for the July 1999 samples were performed using solvent extraction graphite–furnace atomic absorption spectrometry and the analytical methodology has been previously described (Bruland et al., 1979; Bruland et al., 2005). The February 2003 and June 2004 dissolved trace metal data were determined using a modification of methodology reported by Ndung'u et al. (2003). The method employed an iminodiacetate resin (Toyopearl AF-Chelate 650 M, Tosohaas) in a flow injection (FI) system in-line with HR-ICP-MS detection. Acidified samples were UV-oxidized for 30 min prior to analysis. Trace metals were then concentrated on the resin at the appropriate pH and eluted with 1 M $QHNO_3$ (Willie et al., 1998; Warnken et al., 2000; Willie et al., 2001; Ndung'u et al., 2003). The filtrates were loaded onto the resin

column for 2 min for medium resolution analytes (^{56}Fe, ^{59}Co, ^{63}Cu, and ^{66}Zn) at a pH of 5.5 with an ammonium acetate buffer and 30 s for low resolution analytes (^{55}Mn, ^{111}Cd) at a pH of 8.9 with an ammonium chloride buffer in separate analyses (Hurst and Bruland, 2007). In low resolution, ^{55}Mn exhibited a blank of 0.24 ± 0.03 nM due to spectral interferences (Table 1); however, the blank value was negligible with respect to the concentrations found in the samples.

Reference materials were analyzed to determine the accuracy of both the particulate and dissolved trace metal methodology. Five to ten milligrams samples of river sediment (SRM 1645, National Institute of Standards and Technology, USA) and marine sediment (BCSS-1, National Research Council of Canada) were placed on PCTE filters and folded prior to digestion. All particulate trace metal values were within the standard error of the certified values, with the exception of the Al and Mn recoveries in BCSS-1, which were approximately 80% of the certified values. National Research Council of Canada Coastal Atlantic Seawater Standard (CASS-3) and representative California coastal water were used as continuing standards throughout the analytical run for dissolved trace metals. In all cases, the measured CASS-3 values were within the 95% confidence interval (Table 1). The blank values for the dissolved trace metal analyses (acidified Milli-Q™ water, pH 1.7) are also listed in Table 1.

3. RESULTS AND DISCUSSION

3.1. Hydrographic and nutrient data of end members

3.1.1. Identification of end members

The hydrographic and nutrient data were used to identify water masses within the Gulf of the Farallones. The temperature-salinity and nutrient-salinity plots generated from surface transect data collected in July 1999 and June 2004 clearly illustrate the existence of three contributing end members: (1) cold, freshly upwelled water, (2) the less-saline waters of the San Francisco Bay plume, and (3) warm surface waters of coastal California (Fig. 2). The surface water sampling in July 1999 characterized the freshly upwelled water as cold (9.2 °C), highly saline (33.9), and nutrient-rich (nitrate ∼30 μM, silicic acid ∼45 μM). The San Francisco Bay plume is recognized by its lower salinity (32.7), warmer temperature (12.6 °C), and moderately high nutrient concentrations (nitrate ∼20–23 μM, silicic acid ∼33–37 μM). The coastal California surface water is identified by its relatively warm temperature (13.4 °C), high salinity (33.75), and low nutrients (nitrate ∼1 μM, silicic acid ∼5–6 μM). The triangulation of the temperature vs. salinity data in July 1999 (Fig. 2a) is an indication of the mixing that occurs in the region between these water masses. Furthermore, the data in Fig. 2b–c suggest that the uptake of dissolved nutrients by phytoplankton leads to the nitrate and silicic acid concentrations found in the nutrient-depleted California coastal waters, which are in the same concentration range as data previously reported in the California Current (Castro et al., 2002). The June 2004 results demonstrate a similar pattern (Fig. 2d–f), but with

Table 1
Analysis of total dissolved trace metals in CASS-3 (medium resolution analytes, $n = 10$; low resolution analytes, $n = 8$) and in blanks composed of acidified Milli-Q™ to pH 1.7 (medium resolution, $n = 19$; low resolution, $n = 14$)

Element	CASS-3 reference material (nM)[a]		Method blank (nM)[b]
	Measured	Certified	
Fe	21.3 ± 0.9	22.6 ± 2.1	0.15 ± 0.04
Co	0.73 ± 0.07	0.70 ± 0.11	0.004 ± 0.001
Cu	8.6 ± 0.8	8.2 ± 0.6	0.031 ± 0.017
Zn	18.4 ± 1.5	19.0 ± 2.7	0.041 ± 0.021
Cd	0.28 ± 0.02	0.27 ± 0.01	0.051 ± 0.027
Mn	49.7 ± 0.3	44.9 ± 4.6	0.24 ± 0.03

[a] Uncertainty within the 95% confidence interval.
[b] Standard deviation of replicate measurements.

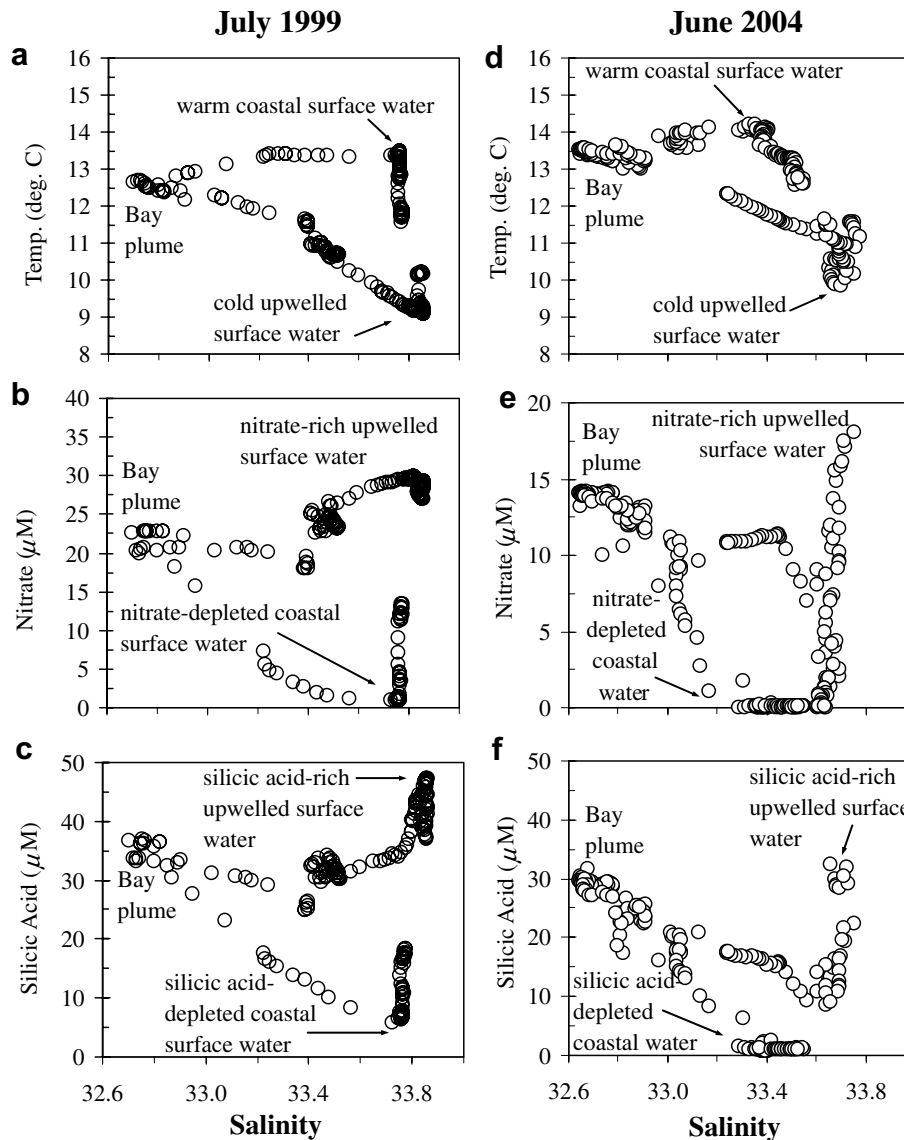**July 1999**   **June 2004**

Fig. 2. Temperature and dissolved nutrients vs. salinity plots from July 1999 (Transect A and B) and June 2004 (Transects A and B) illustrating mixing lines between three distinct end members. The (a) temperature, (b) nitrate, (c) silicic acid in July 1999 and (d) temperature, (e) nitrate, and (f) silicic acid in June 2004 are plotted against salinity.

slightly lower salinities and slightly higher temperatures for each water mass.

In June 2004, the out-flowing ebb tide plume from San Francisco Bay was separated from the coastal waters by an abrupt frontal boundary at 122.66°W, and was defined by the hydrographic and nutrient data (Fig. 3). As the plume was entered across this front, the salinity decreased from 33.3 to 32.6 and temperature increased from 12.3 to 13.5 °C. The dissolved nutrient concentrations in the plume ranged from 25 to 32 μM for silicic acid, 13–14 μM for nitrate, and 1.2–1.4 μM for phosphate. Surface upwelled waters increased the salinity to almost 33.8, lowered the temperature to 9.8 °C, and increased the dissolved nutrient concentrations to 32 μM silicic acid, 22 μM nitrate, and 2 μM phosphate. The July 1999 nutrient and temperature data in both the upwelled water

(maximum salinity of 33.9, minimum temperature of 9.1 °C, 47 μM silicic acid, 29 μM nitrate, and 2.8 μM phosphate) and plume water (minimum salinity of 32.7, maximum temperature of 13.4 °C, 37 μM silicic acid, 23 μM nitrate, and 1.8 μM phosphate) were similar to the June 2004 values (Fig. 4).

The hydrographic conditions and nutrient concentrations in the Gulf of the Farallones differed in winter compared to summer with a decrease in temperature (12.9 to 12.3 °C) and salinity (32.9 to 30.2) in the plume relative to coastal waters (Fig. 5). These data reflect the influence of the Sacramento–San Joaquin Rivers into San Francisco Bay. The nutrient concentrations in the plume waters during February 2003 had maximum values of 34 μM for silicic acid, 9 μM for nitrate, and 1.1 μM for phosphate. These data differed from summer only by a decrease in the nitrate
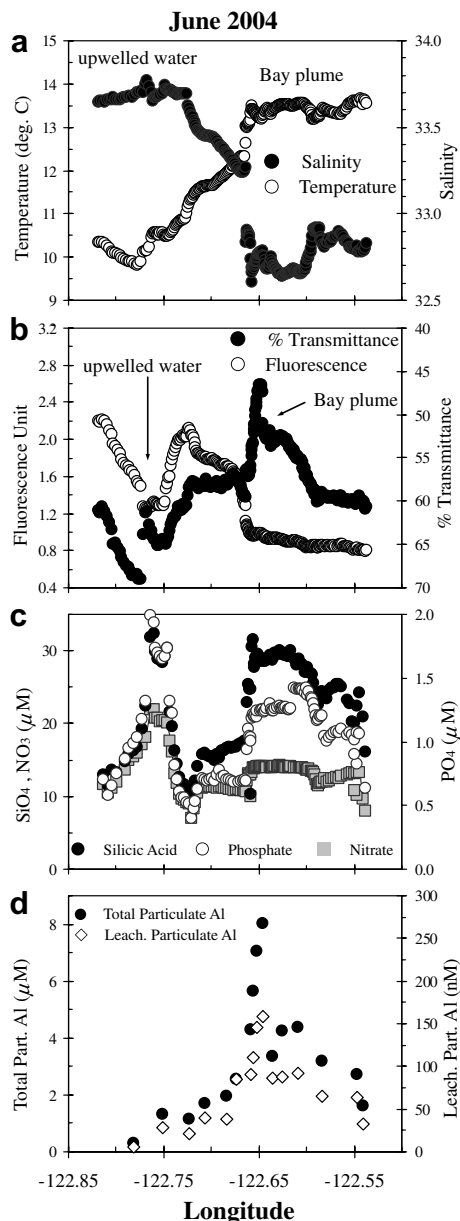
Fig. 3. Surface transect data collected in June 2004 (Transect A) that includes: (a) temperature and salinity, (b) % transmittance and fluorescence units, (c) dissolved nutrients (nitrate, silicic acid, and phosphate), and (d) total and leachable particulate Al.

concentration. Upwelled surface waters were not observed during February 2003.

3.1.2. Stoichiometric comparison of nutrients in plume and upwelled waters

Nutrients in the upwelled and plume waters during July 1999 and June 2004 (Transect A) exhibited a stoichiometric resemblance to one another (Figs. 3 and 4). First, the dissolved nutrient concentrations within the plume were very similar to concentrations in upwelled waters, and second, within the plume there was only a slight enrichment of phosphate and silicic acid relative to nitrate. Using the maximum values in each end member, the July 1999 data

showed nitrate: phosphate concentration ratios of 12.8 in the plume and 10.4 in upwelled waters, which agree well with the June 2004 nitrate:phosphate concentration ratios of 10.4 in the plume and 10.9 in upwelled waters. The July 1999 nitrate:silicic acid concentration ratio was 0.62 in both the plume and upwelled waters, and agreed with the 0.67 ratio found in upwelled water in June 2004. Although the silicic acid concentration was the same in both the plume and upwelled waters ($\sim$32 μM) in June 2004, the maximum nitrate concentration in the plume was markedly lower and resulted in nitrate:silicic acid concentration ratios of 0.45. The February 2003 ratios in the plume were 8.4 for nitrate: phosphate and 0.26 for nitrate:silicic acid (Fig. 5). The nutrient concentration ratios in February 2003 suggest that the plume waters contain decreased amounts of nitrate relative to riverine sources of silicic acid, likely a consequence of less diagenetic inputs of nitrogen from estuarine sediments during the winter period.

The comparison of these ratios suggests that the discharge from San Francisco Bay, containing both anthropogenic sources of phosphate and nitrate along with naturally-occurring nutrients (primarily silicic acid) from freshwater inputs, resembles the nutrient-rich upwelled waters that drive productivity along the California coast in the spring–summer–fall months. This characteristic of plume waters may be altered to look more like upwelled waters at certain times by the inflow of upwelled coastal water into the estuary on the flood tide. Flegal et al. (1991) suggested that the primary source of dissolved Cd, a nutrient-type trace metal (Bruland, 1980), in San Francisco Bay during spring–summer was from coastal upwelled water that had entered the Bay on a flood tide. However, San Francisco Bay has its own sources and internal cycling of nutrients and these anthropogenic sources affect the stoichiometric balance of the nutrient concentrations in the plume. Also, the enriched levels of nutrients in the plume relative to coastal waters increase in proportion at approximately a Redfield ratio. The fact that anthropogenic concentrations of nitrate and phosphate in the plume waters relative to silicic acid were sufficient to create a stoichiometric balance that was comparable to the natural stoichiometric ratio found in upwelled water is in contrast to the effects on nutrient inputs to coastal waters by other well-studied plume systems such as those of the Columbia and Mississippi Rivers. The low levels of nitrate and high concentrations of silicic acid in the waters discharged from the Columbia River estuary leave excess silicic acid to remain in the California current (Aguilar-Islas and Bruland, 2006; Lohan and Bruland, 2006), while the nutrient-enriched discharge from the Mississippi River has a large excess of nitrate relative to silicic acid, and creates conditions within the Gulf of Mexico that may be limited by nitrate, phosphate, or silicic acid concentrations (Dortch and Whitledge, 1992; Rabalais et al., 2002; Sylvan et al., 2006). In the Gulf of the Farallones, summer data show only a 1–6 μM excess of silicic acid and about 0.5 μM phosphate in the surface waters once nitrate had been depleted to less than 1 μM in coastal waters (Fig. 2).

The dissolved nutrient distributions in the Gulf of the Farallones were affected by both conservative mixing
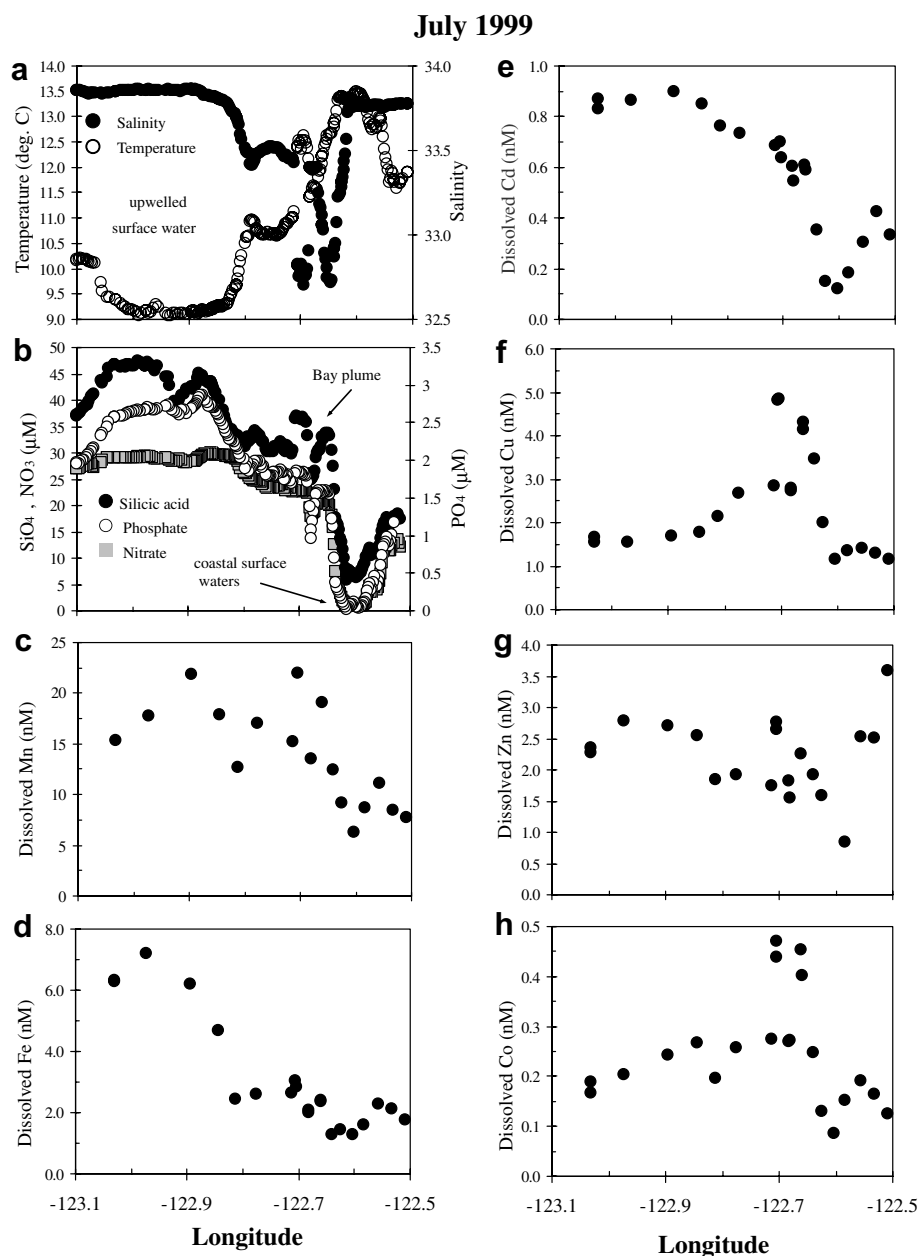
July 1999

Fig. 4. Surface transect data collected in July 1999 that includes: (a) temperature and salinity, dissolved (b) nutrients (nitrate, silicic acid, and phosphate), (c) Mn, (d) Fe, (e) Cd, (f) Cu, (g) Zn, and (h) Co.

(Fig. 2) and removal of nutrients by phytoplankton (Fig. 3). Although phytoplankton blooms are a regular occurrence in San Francisco Bay (Cloern, 1996; Luengen et al., 2007), the chlorophyll minimum in June 2004 was in the plume and at a maximum between the plume and upwelled waters (Fig. 3b). The stoichiometric drawdown of nitrate, silicic acid, and phosphate in a phytoplankton bloom can be estimated using the C:N:P Redfield ratio of 106:16:1 and the ratio of N:Si assimilation by diatoms of about 1:1 (Brezezinski, 1985). Both upwelled waters and the plume deliver dissolved nutrients to the surface waters at ratios close to those mentioned, with the exception of silicic acid and phosphate enrichment relative to nitrate in the plume. Given the dissolved nutrient concentrations in source waters and minimum values in the productive coastal waters during June 2004 (7.0 μM nitrate, 0.40 μM phosphate, and 9.4 μM silicic acid), it is uncertain whether nitrate or phosphate becomes the limiting nutrient within this extended estuarine/upwelling regime (Fig. 3c). However, the depleted nitrate and excess phosphate concentrations measured in surface coastal waters in February 2003 and July 1999 indicate that the Gulf of the Farallones is most likely a nitrate-limited system (Figs. 4b and 5b).
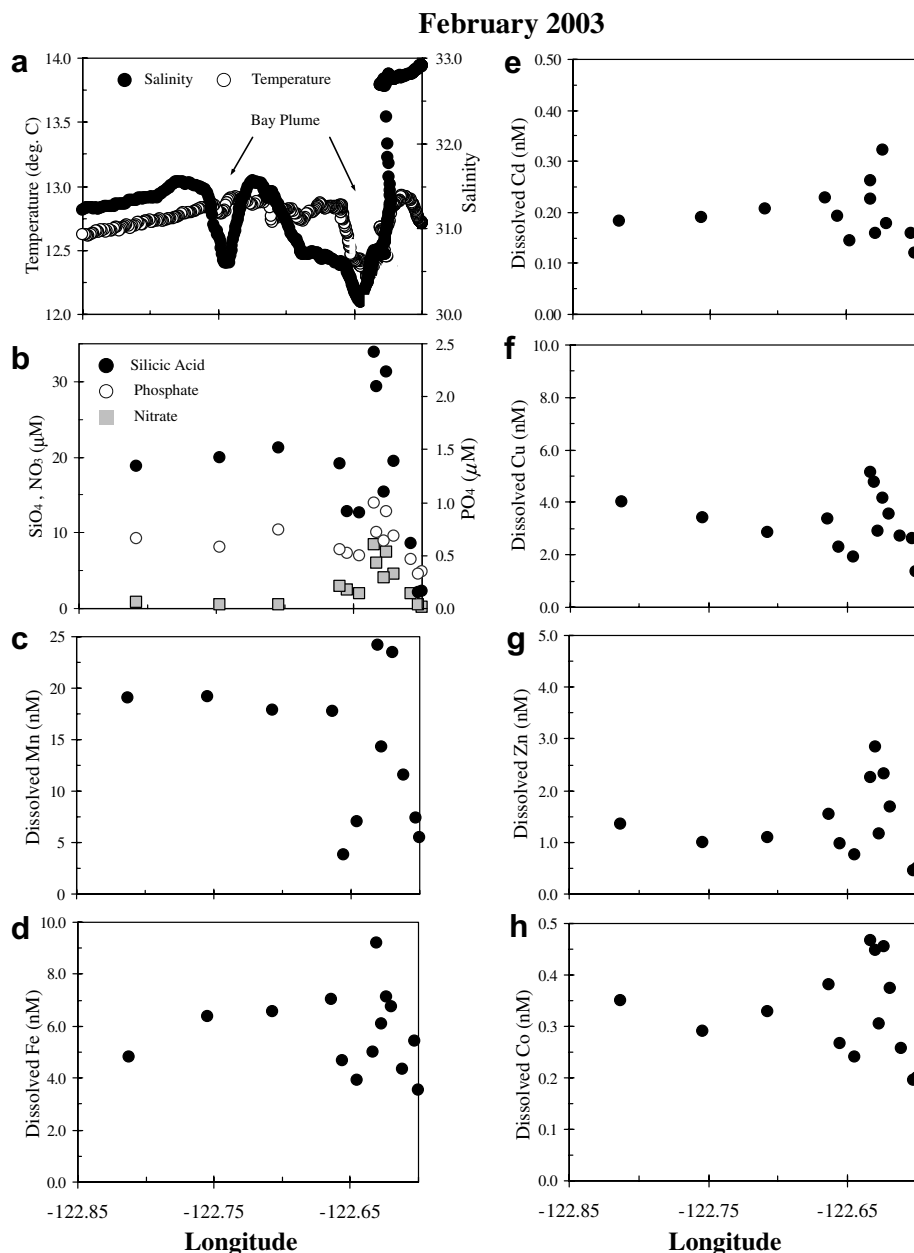
February 2003

Fig. 5. Surface transect data collected in February 2003 that includes: (a) temperature and salinity, dissolved (b) nutrients (nitrate, silicic acid, and phosphate), (c) Mn, (d) Fe, (e) Cd, (f) Cu, (g) Zn, and (h) Co.

3.2. Particulate element distributions

3.2.1. Total particulate elements in san francisco bay plume

Particulate element concentrations in the 0.4–10 μm and >10 μm size-fractions were determined in February 2003 and June 2004 and further separated into leachable and refractory fractions (Figs. 6 and 7). The total particulate element distributions in the plume during June 2004 varied inversely with transmittance for all trace metals with the exception of particulate Cd, which varied with the particulate phosphorus distribution and fluorescence intensity ($P < 0.05$). The total particulate metal concentrations, with exception of Cd, in the upwelled waters and productive

coastal waters were low relative to the elevated concentrations in the plume. The maximum total particulate concentrations in the plume during June 2004 for Al (8000 nM), Mn (85 nM), Fe (2600 nM), Co (0.9 nM), Cu (2.4 nM), Zn (6.4 nM), and Pb (0.6 nM) were found close to the well-defined frontal boundary between the plume and the productive coastal waters (Figs. 3 and 6). The total particulate Cd concentration was at a minimum in the plume (0.06 nM), implying that Cd in the particulate phase is associated with phytoplankton biomass rather than the suspended particulate load originating from San Francisco Bay. This is consistent with the fact that Cd has a relatively low abundance in the earth's crust, is known to vary with
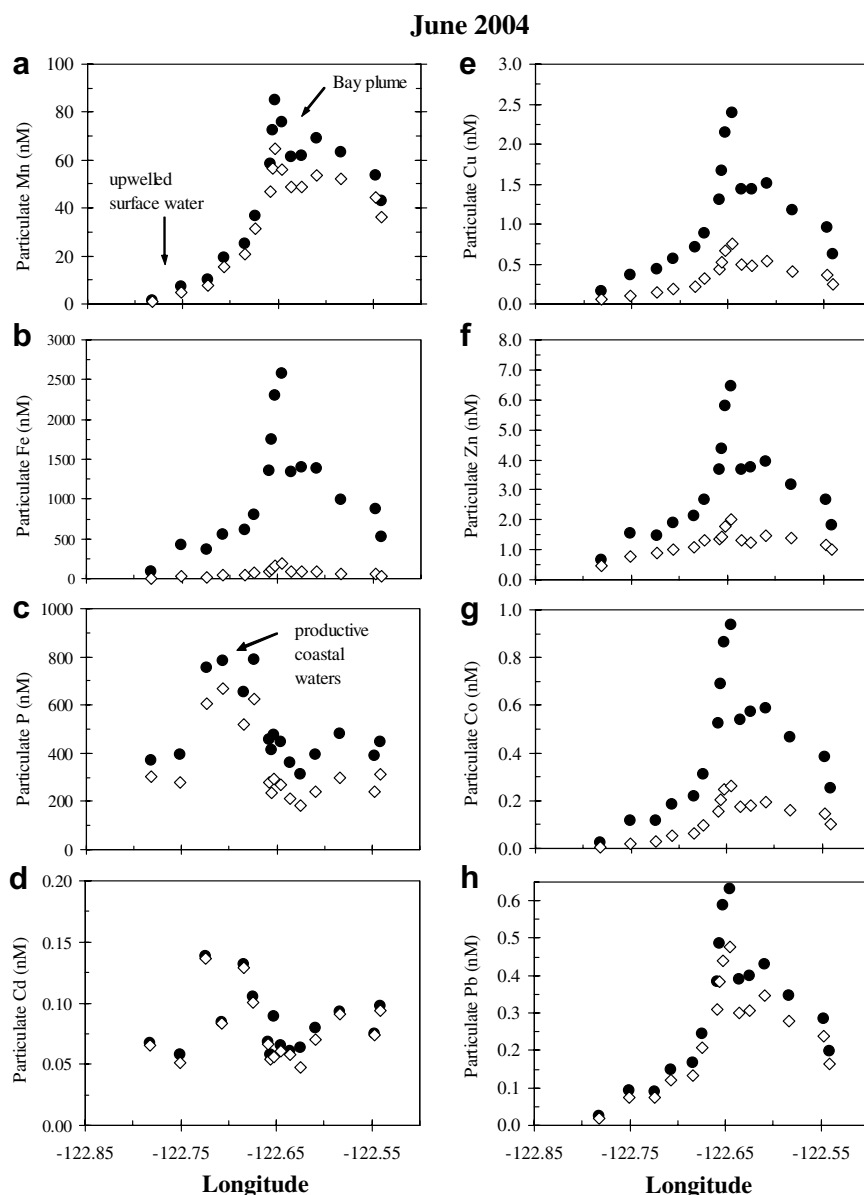
June 2004

Fig. 6. Spatial distributions of (a) Mn, (b) Fe, (c) P, (d) Cd, (e) Cu, (f) Zn, (g) Co, and (h) Pb in the >0.4 μm size-fraction and represented as total particulate (●) and leachable particulate (◇) elements along Transect A in June 2004.

phosphate, and is incorporated into phytoplankton biomass (Bruland, 1980). In February, maximum total particulate concentrations for Al (4300 nM), Mn (90 nM), Fe (1800 nM), Co (0.9 nM), Cu (2.9 nM), Zn (7.7 nM) were found in the plume (Fig. 7). A maximum particulate Pb concentration of 0.2 nM was measured in a subset of samples clustered in the plume.

The particulate element data collected in June 2004 and February 2003 for the different size-fractions in the plume suggests that temporal variability influences the partitioning of certain elements. In February 2003, 55–60% of the particulate Al and Fe was in the 0.4–10 μm size-fraction, while the partitioning of these elements in the plume during June 2004 indicated that only ~35% of the particulate Al and Fe were in this smaller size-fraction. The shift in the rel-

ative abundance of these elements to the larger size-fraction (>10 μm) from winter to summer may be an indication of the source of the particles, with the winter conditions influenced more by the fluvial inputs from the Sacramento–San Joaquin Delta, which leads to a shorter residence time in the northern reaches of San Francisco Bay and a greater transport of clay particles through the estuary. Particulate matter associated with the plume in summer months is primarily from wind-driven turbulence. It is also possible that the shift in size-fractionation could be attributed to biological packaging/aggregation of small terrigenous particles during the more productive summer period. Yet, the maximum particulate Pb concentration during June 2004 (0.6 nM) relative to February 2003 (0.2 nM) suggests that the source of particles during summer is from the resuspen-
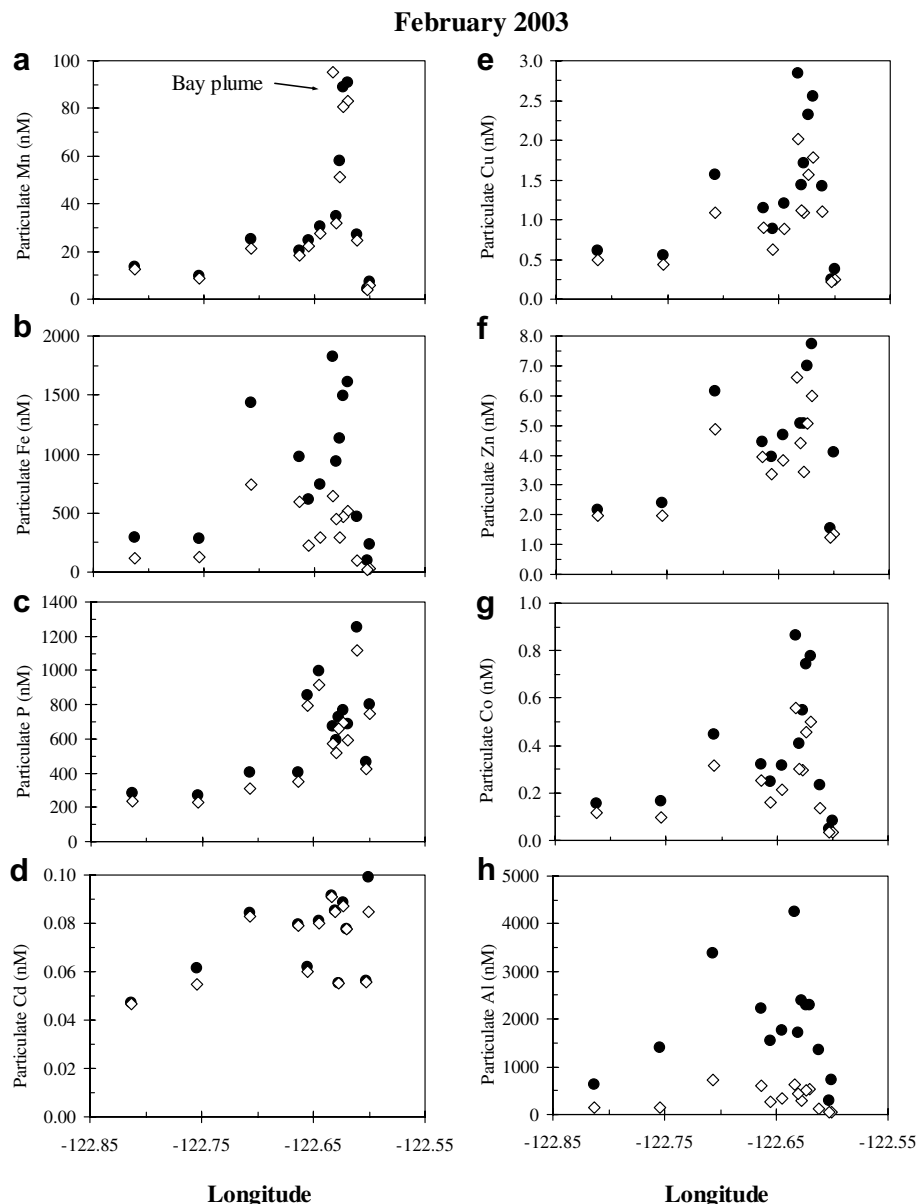
February 2003

Fig. 7. Spatial distributions of (a) Mn, (b) Fe, (c) P, (d) Cd, (e) Cu, (f) Zn, (g) Co, and (h) Al from February 2003 in the >0.4 μm size-fraction and represented as total particulate (●) and leachable particulate (◇) elements.

sion of contaminated sediments in San Francisco Bay. Lastly, since most of the total Pb in the plume was associated with these suspended particles in both the winter and summer, and was more than 5–50 times greater than concentrations found in the coastal waters, particulate Pb could be used as a tracer of the San Francisco Bay plume.

3.2.2. Leachable particulate elements

A major difference between the February 2003 and June 2004 particulate element data was the relative concentration of the leachable particulate fraction, with substantially higher concentrations found in the winter. The leachable particulate trace metal concentrations in the core of the plume during the sampling events (winter 2003 and summer 2004) consisted of: Al (640 and 160 nM), Fe (740 and

190 nM), Mn (95 and 65 nM), Co (0.6 and 0.3 nM), Cu (2.0 and 0.8 nM), Zn (6.6 and 2.0 nM), Cd (0.14 and 0.09 nM), and Pb (0.09 and 0.5 nM) (Figs. 6 and 7). Both particulate Fe and Al show a relatively high percent leachable fraction (>0.4 μm) in the winter period with values of 37% and 20%, respectively, compared to 6% and 2% of particulate Fe and Al as leachable in the summer. Previous work has shown that the 25% acetic acid leach is a mild extraction of chemically labile Fe associated with biomass, whereby particulate samples collected within a large diatom bloom were more than 90% leachable for Mn, Co, Cu, Zn, and Cd, but only 6% leachable for Fe (Hurst and Bruland, 2007). The work also suggested that this fraction is bioavailable to phytoplankton, but that the acetic acid-leach is unable to remove all bioavailable forms of Fe incorporated

in the particles. Consequently, the operationally-defined refractory fraction includes both non-leachable material associated with terrigenous particles and possibly a substantial amount of biogenic particulate material.

Although the data suggest that the total amount of particulate Fe in the plume of the ebb tide from San Francisco Bay may not be significantly different from winter to summer, 1800 and 2600 nM, respectively, the percent that was leachable shifted from 37% to 6% respectively. It has been suggested that this leachable particulate Fe is deposited on the shelf region during winter months and made available for primary productivity during spring and summer upwelling events (Johnson et al., 1999;Bruland et al., 2001;Chase et al., 2007). The differences in leachable particulate Fe between the two sampling events can be explained by considering the seasonality of particle residence times in the estuary. The relatively short residence time of particles in the winter results in a higher leachable particulate fraction reaching coastal waters. Low flow conditions in the

summer allow the particles to age and, consequently, the Fe coatings are removed prior to reaching the Gulf of the Farallones. In addition, work by Buck et al. (2007) has shown the importance of strong organic ligands in solubilizing the leachable particulate Fe within the Gulf of the Farallones. During winter flood events, the large suspended load containing leachable particulate Fe is delivered to the estuary where it overwhelms the ability of the strong organic ligands to solubilize the Fe. These ligands, which dictate dissolved Fe concentrations in estuarine and marine systems (Rue and Bruland, 1995; Cullen et al., 2006; Gerringa et al., 2007; Buck et al., 2007), quickly become saturated and solubilize only a fraction of the leachable particulate Fe within the water column. This leaves a large percentage of the leachable particulate Fe to be deposited on the continental shelf where it can be reintroduced to the surface waters during upwelling events. In the summer, the suspended particles delivered to the Gulf of the Farallones have less acid-leachable Fe associated with them as a
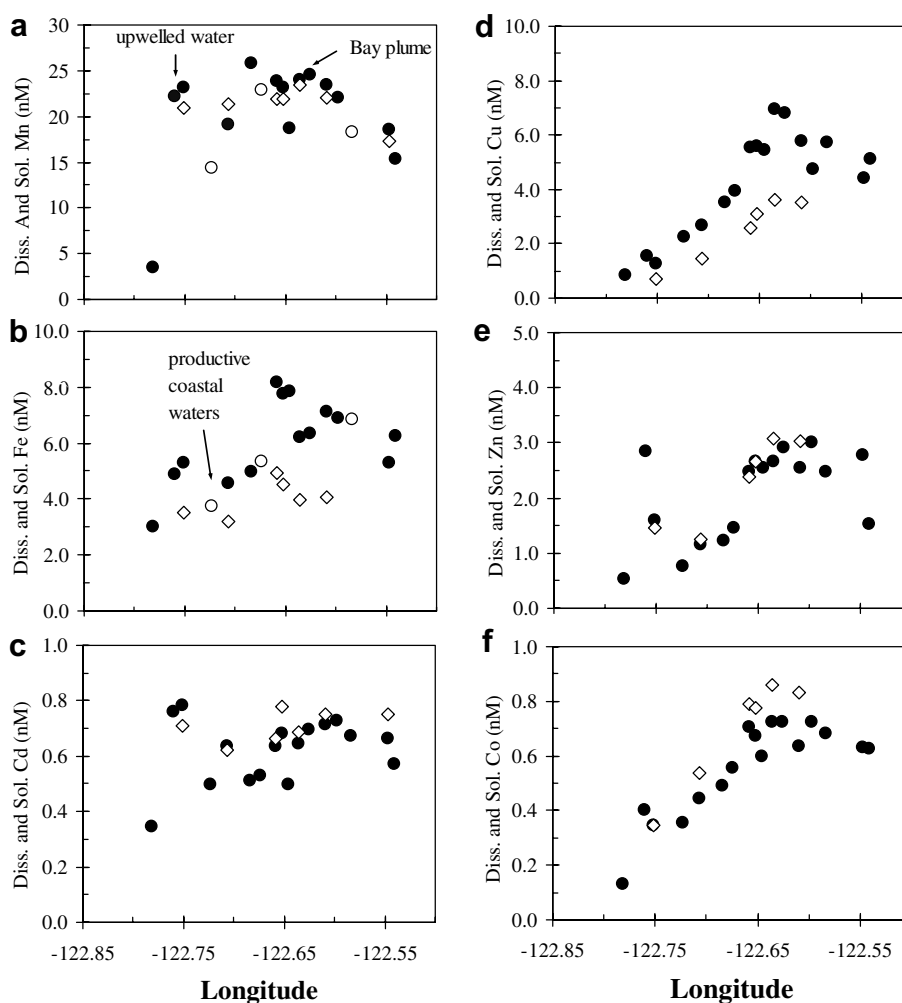
June 2004

Fig. 8. Dissolved trace metal distributions of (a) Mn, (b) Fe, (c) Cd, (d) Cu, (e) Zn, and (f) Co along Transect A in June 2004. The ● represents the total dissolved concentration (<0.4 μm) and ◇ represents the soluble concentration (<0.03 μm). The ○ in (a) and (b) represents dissolved concentrations from samples collected using a 0.45 μm flow-through filter.

result of the Fe binding ligands gradually solubilizing readily leachable particulate Fe during the long residence time in the San Francisco Bay estuary. The argument that the presence of strong organic ligands dictates the solubilization of Fe in coastal waters is strengthened by the fact that the maximum dissolved Fe concentration within the plume during summer and winter only varied between 3 and 9 nM while the leachable particulate concentrations varied between 190 and 740 nM, respectively.

The leachable particulate concentration of trace metals other than Fe also showed seasonal variability. Like Fe, contaminant particulate trace metals such as Zn, Cu, and Co were present at higher percentages within the leachable particulate fraction in the winter compared to summer. However, unlike Fe, these leachable particulate trace metals are supplied to the shelf in such low quantities that their contributions to dissolved trace metal concentrations during upwelling are small when compared to the concentrations of dissolved trace metals already existing in the subsurface waters (Bruland, 1980).

3.3. Dissolved trace metal distributions

Dissolved trace metal data were collected in July 1999 (Fig. 4), February 2003 (Fig. 5), and June 2004 (Fig. 8). In June 2004, the dissolved (<0.4 μm) samples were further fractionated into a soluble (<0.03 μm) fraction. The total dissolved concentrations found in the plume during June 2004 were in the nanomolar range for Fe (6–8 nM), Mn (20–25 nM), Zn (~3 nM), and Cu (5–7 nM), and at the sub-nanomolar levels for Cd (0.6–0.8 nM) and Co (0.6–0.8 nM). Dissolved trace metal concentrations in the upwelled waters were elevated for Mn (23 nM), Fe (5.3 nM), Cd (0.8 nM), and Zn (2.8 nM) relative to the near-shore and productive coastal waters, while Cu (1.6 nM) and Co (0.4 nM) were only marginally different from surrounding surface waters (Fig. 8). The soluble fraction for these trace metals are also plotted in Fig. 8, and only Fe and Cu were observed to have a significant colloidal fraction (30–50%). All other dissolved trace metals (Mn, Zn, Cd, and Co) were found only sparingly (<10%) within the colloidal fraction.

The July 1999 dissolved trace metal data exhibited slightly lower values in the plume and similar results in surface upwelled waters relative to June 2004 (Fig. 4). The total dissolved concentrations measured in the plume varied for Fe (2–4 nM), Mn (15–22 nM), Zn (2–3 nM), Cu (3–5 nM), Cd (0.5–0.7 nM), and Co (0.4–0.5 nM). The total dissolved concentrations in upwelled waters during July 1999 reached maximum values for Fe (7.2 nM), Mn (22 nM), Zn (2.8 nM), and Cu (1.7 nM), Cd (0.9 nM), and Co (0.3 nM).

In February 2003, the dissolved trace metal concentrations in the plume were Fe (5–9 nM), Mn (18–33 nM), Zn (1–3 nM), and Cu (3–4 nM), Cd (~0.2 nM), and Co (0.25–0.45 nM) (Fig. 5). The dissolved concentrations of Mn, Fe, Zn, and Cu were similar to the values measured in the plume during June 2004, while Cd was markedly lower in average concentration during the winter and implies the absence of upwelling.

In all of the sampling periods, the dissolved Cu and Co concentrations were markedly higher in the San Francisco Bay plume compared to upwelled or coastal waters and allows these trace metals to be used as tracers of the plume. Given the correlation of Cu and Co with salinity, it is plausible to extrapolate the dissolved Cu and Co into the central portion of San Francisco Bay. For example, using the correlation between Cu and Co concentrations and salinity in Fig. 9, concentrations could be estimated for waters at the Golden Gate (i.e., mouth of San Francisco estuary) and compared to concentrations from three sampling events in 1989 (Flegal et al., 1991). Using the average salinity (31.0) at the Golden Gate from 1989, the Cu and Co concentrations are predicted to be 14 and 1.4 nM, respectively. These values agree with the average values of 14 nmol kg^{-1} for Cu and 1.1 nmol kg^{-1} for Co reported by Flegal et al., 1991. Although conservative mixing is evident between the Gulf of the Farallones and San Francisco Bay, extrapolation to lower salinities found in the northern reaches of San Francisco Bay and south San Francisco Bay is complicated due to the fact that these regions contribute differently in terms of contaminant trace metal concentrations and tidal flow (Flegal et al., 1991; Cheng et al., 1993) (Fig. 10). South San Francisco Bay generally has higher dissolved contaminant trace metal concentrations relative to northern regions of the Bay, particularly for dissolved cobalt, which is compounded by less fresh water inputs and a longer residence time of the water in this portion of the Bay.

3.4. Comparison of fractionated trace metals in end members

3.4.1. Dissolved (soluble vs. colloidal) trace metals

The trace metal data in June 2004 showed a shift in fractionation between soluble and colloidal forms within the productive coastal waters compared to source waters, where a lower percentage was found in the colloidal fraction for most metals (Fig. 11a). Approximately 50% of dissolved Fe and Cu in the plume and upwelled waters was colloidal. In the productive coastal waters, the dissolved Fe and Cu concentrations decreased relative to source waters and could be attributed to the apparent disappearance of the colloidal fraction. It is not certain whether this decrease in colloidal Fe and Cu is solely due to aggregation processes or if the colloidal fraction is becoming solubilized due to the production of organic ligands within the phytoplankton bloom. Previous results from laboratory incubation experiments and field work have suggested that colloidal Fe is a readily available to phytoplankton (Nishioka and Takeda, 2001; Nishioka et al., 2001b; Chen et al., 2003), while others have argued that colloidal Fe is thermodynamically inert and not likely to be bioavailable (Cullen et al., 2006). The data in Fig. 11a suggest that the colloidal fraction is a biologically active reservoir for Fe and Cu.

Colloidal trace metal data in the San Francisco estuary from January 1994 were previously reported using a cross-flow filtration system with a cutoff of 10 kDa/0.2 μm for colloids (Sañudo-Wilhelmy et al., 1996). At high salinities within San Francisco Bay, Sañudo-Wilhelmy et al. (1996) reported ~40% colloidal Fe, <10% colloidal Mn and Cu, <3% colloidal Zn, and essentially no colloidal Cd. The plume data herein was consistent with these data
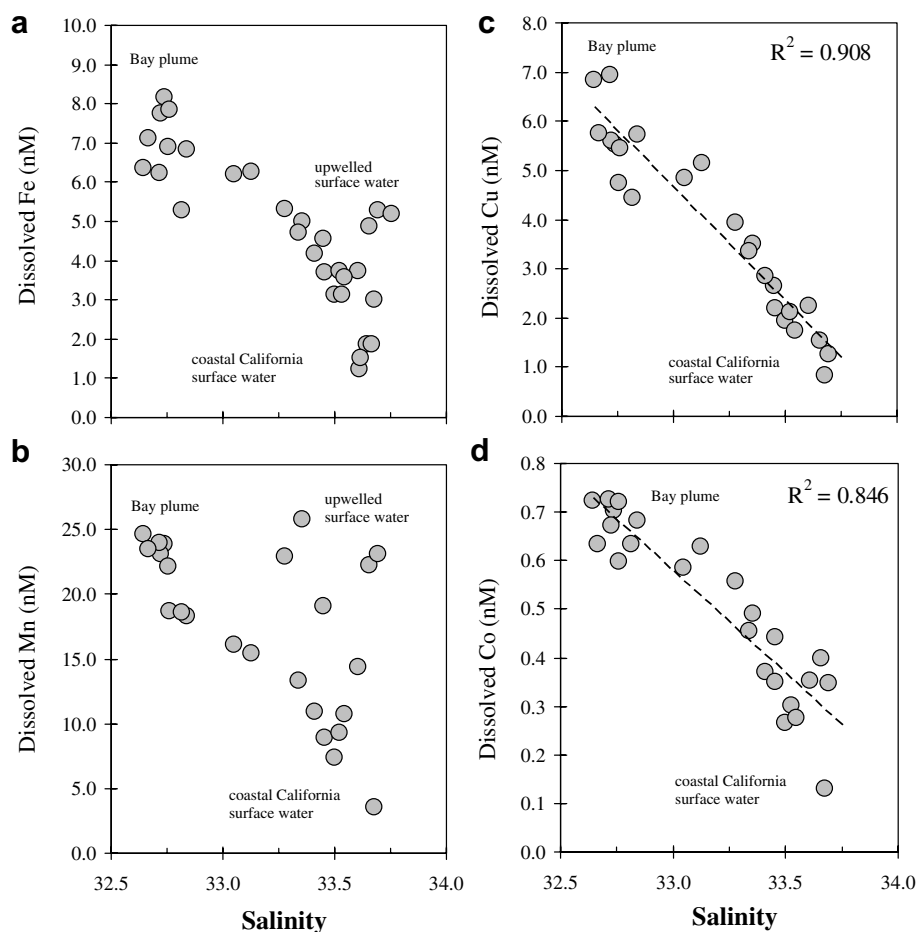
Fig. 9. Property-salinity plots of dissolved (a) Fe, (b) Mn, (c) Cu, and (d) Co within the Gulf of the Farallones.

with exception to a larger estimate of colloidal copper in the plume. It is possible that the resuspension of the sediments inside the estuary during summer months contributed to an increased amount of colloidal copper. The June 2004 data also found a higher percent colloidal fraction for other contaminant trace metals such as Zn (6%) and Cd (3%) (Fig. 11a). However, the dissolved trace metal fractionation of estuarine waters compared well considering the differences in techniques, sampling location, and the selection of an operationally-defined cutoff.

3.4.2. Bioactive trace metals (dissolved vs. leachable particulate)

The comparison between dissolved and leachable particulate trace metal distributions in end member water masses revealed a fractionation shift between February 2003 and June 2004 (Fig. 11b). Assuming bioactive trace metal concentrations are the sum of dissolved and leachable particulate metals, the leachable particulate Fe fraction constituted 92% of the total bioactive Fe in the plume, 85% in upwelled waters, and 74% in the productive coastal waters (Fig. 11b). The shift in the partitioning to a higher percentage of dissolved species within the productive coastal waters only occurs with Fe and is due to a substantial and disproportionate decrease in leachable particulate Fe. This

decrease can either be a consequence of Fe assimilation by the biomass and the conversion of leachable particulate Fe into the operationally-defined refractory fraction, or removal of this fraction through the aggregation and settling of particles. The nitrate drawdown in the productive coastal waters would require more Fe than is present in the dissolved phase and suggests that leachable particulate Fe is used to meet biological requirements.

Prior work has shown that the Redfield ratio can be extended to include the trace metal requirements of phytoplankton (Bruland et al., 1991) and has been estimated to be C (106): N (16): P (1): Fe (0.005): Zn (0.002): Mn, Cu, Cd (0.0004). This ratio was based upon the analysis of coastal phytoplankton biomass samples collected in Monterey Bay (Martin and Knauer, 1973). Using the average dissolved trace metal-to-phosphate concentrations (Me:P) from all sampling events, the ratio was estimated to be P (1): Fe (0.005): Zn (0.002): Mn (0.02): Cu (0.003): Cd (0.0004) in the San Francisco Bay plume and P (1): Fe (0.004): Zn (0.001): Mn (0.02): Cu (0.001): Cd (0.0006) in upwelled waters. Both water masses have dissolved Me:P ratios similar to those of phytoplankton biomass, with the waters of the San Francisco Bay plume containing a higher Me:P ratio for essential micronutrients such as Fe and Zn. Incoming seawater, possibly influenced by upwelled waters
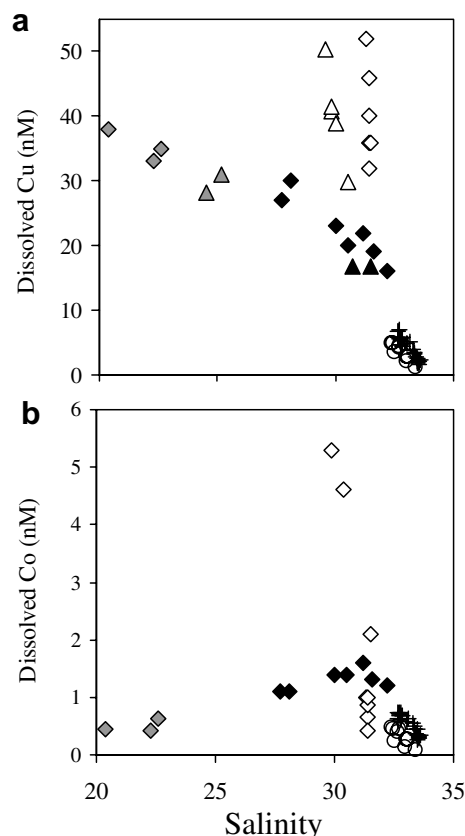
Fig. 10. Property-salinity plots illustrating conservative mixing of (a) Cu and (b) Co from the San Francisco Bay estuary into the Gulf of the Farallones during summer months. The northern reaches of San Francisco Bay (gray), south San Francisco Bay (white), and Central San Francisco Bay (black) are noted. Data from the Gulf of the Farallones collected in July 1999 (○) and June 2004 (+) are also plotted versus salinity. The multi-shaded ◇ represent San Francisco Bay data from August, 1989 (Flegal et al., 1991) and the multi-shaded △ represent copper data from June and July, 2001, which were generated from samples collected by Bruland.

in spring–summer months, becomes enriched with dissolved Fe, Zn, Cu and Co while in the estuary and this alteration of the water is observed in the Me:P ratios found in the plume. With respect to the requirements of coastal diatoms, the inclusion of the leachable particulate trace metal fraction creates an excess of trace metal micronutrients relative to phosphate and nitrate.

3.5. Relative contribution of dissolved nutrients and trace metals by the plume

The flux of dissolved nutrients and trace metals from the San Francisco Bay plume and upwelled waters were estimated in order to determine contributions of each source to the highly productive coastal waters of the Gulf of the Farallones (Table 2). The contributing flows of the plume and upwelled waters were calculated with several assumptions. First, the outflow of San Francisco Bay waters to the Gulf of the Farallones is most significantly influenced by the tides, but also is influenced by fresh water inputs.
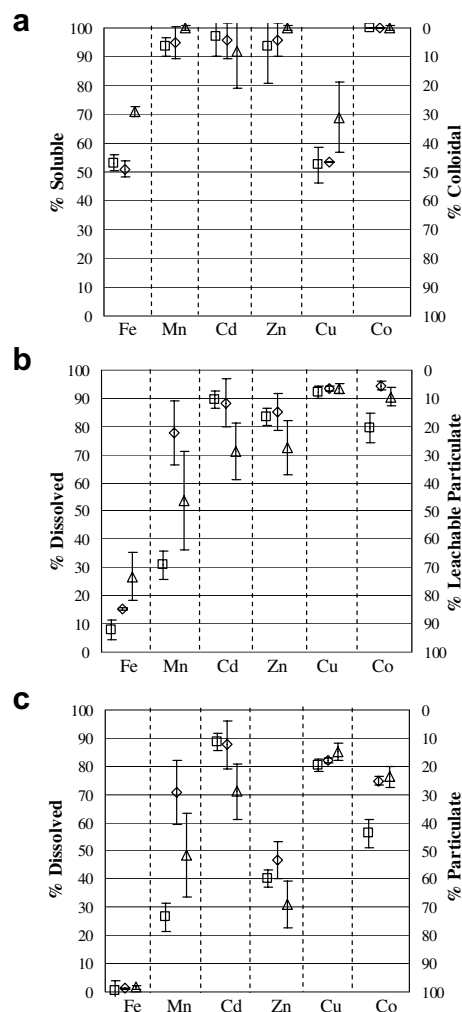

Fig. 11. Plots illustrating the percent trace metals (Fe, Mn, Cd, Zn, Cu, and Co) partitioned between two fractions consisting of: (a) soluble vs. colloidal trace metals (dissolved fraction), (b) dissolved vs. leachable particulate trace metals (bioactive fraction), and (c) dissolved vs. total particulate metals. The three separate end members are plotted, where □ represents San Francisco Bay plume ($n = 10$), ◇ represents upwelled surface waters ($n = 3$), and △ represents the productive coastal waters ($n = 5$). Data were compiled using the data collected in June 2004 along Transect A and B.

The tidal prism for San Francisco Bay has been estimated at 1.5×10^9 m^3 (Cheng et al., 1993). However, much of the water that flows into the Bay from the Gulf of the Farallones is a remnant of the last tidal cycle. It has been estimated that the amount of "new water" entering through the Golden Gate during the flood tide is 10% of the total volume (Denton and Hunt, 1986). This new water can be translated as an exchange between two water masses and used to calculate the flux of plume constituents. Since only 10% of the tidal prism volume is exchanged (1.5×10^8 m^3 every 12.4 h), the annual average flow of 6.7×10^7 m^3 day^{-1} from the Sacramento–San Joaquin Rivers can not be ignored and is included in the flux estimation (California Department of Water Resources, 1993). Second, the deliv-

Table 2
Average dissolved nutrient (μM) and trace metal (nM) concentrations measured in upwelled waters (July 1999 and June 2004) and the San Francisco Bay plume (July 1999, February 2003 and June 2004) and their estimated flux to surface waters in the Gulf of the Farallones

Constituent	Average concentrations (μM)		Estimated flux (mol s^{-1})		% Contribution of plume constituents relative to upwelling
	Upwelling	Bay plume	Upwelling	Bay plume	
Nitrate	25	15	600	62	10
Phosphate	2.4	1.4	58	5.8	10
Silicic acid	40	35	970	140	15
	Average concentrations (nM)				
Fe	6.2	7.0	0.15	0.029	20
Mn	23	27	0.55	0.11	20
Zn	2.8	3.0	0.068	0.012	20
Cu	1.7	5.3	0.041	0.022	50
Co	0.4	0.6	0.010	0.0025	25
Cd	0.9	0.6	0.022	0.0025	10

ery of upwelled waters along the shelf within the Gulf of the Farallones was estimated at 0.96 m^2 s^{-1} using the average positive upwelling values obtained from the historical upwelling index (1967–2006) at 39°N and 125°W and 36°N and 125°W (see pfeg.noaa.gov/products/PFEL/modeled/indices/upwelling). This is a reasonable estimate for the Gulf of the Farallones at a latitude 37.5°N. The upwelling estimate also assumes a 25 km stretch of coastline where upwelling and plume water masses converge. Given these assumptions, the annual flow of upwelling along the 25 km of shelf was roughly 10 times greater than the exchange of new water from San Francisco Bay.

The percent contribution of constituents from the plume relative to upwelled water (plume/upwelling × 100%) give a rough estimate of the effects that the plume has on the dissolved nutrient and trace metal distributions in the Gulf of the Farallones (Table 2). The contributions of dissolved nutrients varied between 10 and 15%, while Fe, Mn, and Zn were all approximately 20%. The largest contribution from the plume to coastal waters was as dissolved Cu (50%) and Co (25%). Uncertainties in these values are created by (1) the probability that a portion of the plume waters was originally upwelled water (implied by the 10% contribution of Cd from the plume) and (2) the likelihood that contributions from the plume were diluted through conservative mixing between the mouth of the estuary and the point of sampling. The degree of conservative mixing can be estimated by using the property-salinity plots for dissolved Cu and Co in Fig. 9 and assuming a salinity of 31.0 at the mouth of the estuary (Flegal et al., 1991). The calculation yields concentrations at the mouth of the estuary that are roughly twice the values at the sampling point and implies that the gross flux estimates for the plume may be conservatively low.

4. CONCLUSION

The biogeochemical implication of the San Francisco Bay plume in the Gulf of the Farallones is an increased productivity due to the supply of dissolved nutrients and trace metal micronutrients. Also, the delivery of leachable partic-

ulate Fe by the plume during the winter sampling period (37% of total particulate concentration) was significantly higher than the values measured during the summer (6% of total). This leachable particulate Fe, deposited on the relatively broad continental shelf in the winter months, provides a source of dissolved Fe to be upwelled in the spring–summer months. In contrast, the supply of nitrate, phosphate, silicic acid and trace metal micronutrients from upwelled subsurface waters and the resuspension of fluvial inputs from the continental shelf are intermittent and dependent upon sustained northwesterly winds (Fitzwater et al., 2003). While most of the primary production is dependent upon seasonal upwelling, the Gulf of the Farallones is provided dissolved nutrients and trace metals to the surface waters throughout the year from the daily ebb tide flux of the San Francisco Bay plume. This additional and continuous supply of macronutrients and micronutrients can lead to the appearance of Gulf of the Farallones as a sustained high chlorophyll region in satellite images relative to surrounding regions that are only influenced by sporadic coastal upwelling.

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