Tracing Ni, Cu and Zn Kinetics and Equilibrium Partitioning Between Dissolved and Particulate Phases in South San Francisco Bay, CA, Using Stable Isotopes and HR-ICPMS.

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ABSTRACT

Additions of the low occurrence stable isotopes $^{61}$Ni, $^{65}$Cu and $^{68}$Zn were used as tracers to determine the exchange kinetics of metals between dissolved and particulate forms in laboratory studies of natural water and suspended sediments from South San Francisco Bay, CA. Dissolved metal isotope additions were made so that the isotope ratios (rather than total metal partitioning) were significantly altered from initial ambient conditions. Dissolved metal concentrations were determined using an organic ligand sequential extraction technique followed by analysis with high resolution inductively coupled plasma mass spectrometry (HR-ICPMS). Exchangeable particulate concentrations were extracted using a 20% acetic acid leach followed by determination using HR-ICPMS. Equilibrium and kinetic sorption parameters were quantified according to a general model for trace metal partitioning assuming pseudo-first order kinetics. Partition coefficients ($K_D$) were tracked as a function of time over the fortnight experiment. For Ni, Cu and Zn the initial ambient $K_D$ values were found to be $10^{3.65}$, $10^{3.88}$ and $10^{4.52}$ L kg$^{-1}$, respectively. As a result of the dissolved metal isotope additions, the partition coefficients for all three metals dropped and then increased back to near ambient $K_D$ values after 14 days. Curve-fitting concentration versus time profiles from both dissolved and exchangeable particulate data sets allowed determination of kinetic rate constants. The best estimates of forward and backward kinetic rate constants for Ni, Cu and Zn respectively are $k'_f = 0.03, 0.07, 0.12$ d$^{-1}$ and $k_b = 0.13, 0.12, 0.15$ d$^{-1}$. These results predict that sorption equilibria in South Bay should be reached on the order of two weeks for Zn, on the order of three weeks for Cu and on the order of a month for Ni. Together, the dissolved and exchangeable particulate data indicate more sluggish sorption kinetics for Ni than for Cu and Zn and suggest that different chemical forms control the speciation of these three metals in South Bay. Order of magnitude metal sorption exchange rates were estimated using these kinetic results. These calculations indicate that sorption exchange between dissolved and suspended particulate phases can cause dynamic internal cycling of these metals in South San Francisco Bay.
1. INTRODUCTION

The exchange of dissolved trace metals such as Ni, Cu and Zn between solution species and particle surfaces is an important topic for estuarine waters. To date, the majority of studies conducted on suspended particles have focused on the observed fractionation between dissolved and particulate metal concentrations (Kuwabara et al., 1989; Smith and Flegal, 1993; Benoit et al., 1994; Rivera-Duarte and Flegal, 1994; and Sanudo-Wilhelmy et al., 1996). This fractionation, quantified as a distribution coefficient, measures the distribution of different metals between the particulate phase and dissolved species at a given time and location. However, studies seldom address kinetics of the exchange process such as the rate at which metal-particle associations occur, information relevant for metal fate and transport assessments. For example, if there is an input perturbing either the dissolved or suspended particulate phase of a certain metal, at what rate will the system come to a new equilibrium? We would also like to know if there is dynamic exchange occurring between the dissolved and exchangeable particulate metal pools, or if suspended particulate metal is essentially inert with respect to sorption processes on the time scales of sediment resuspension events and particle residence times in the water column. Thus, constraining the kinetics of metal-particle adsorption/desorption reactions in estuarine waters can substantially enhance current understanding of both scavenging and desorption from contaminated particles as important controls on dissolved metal concentrations.

To assess the exchange rates of metals between dissolved and particulate forms, one needs methods to trace the process in such a manner that it adequately simulates natural “ambient” conditions. Most previous studies in the literature of sorption kinetics have involved laboratory experiments using pure phase particles with well characterized surface characteristics and inorganic solution species, the results of which report rapid adsorption rates on the order of
minutes to hours (Atkinson et al., 1972; Anderson and Rubin, 1981; Hayes and Leckie, 1986). Due to the heterogeneous nature of most natural suspended material, however, rate constants determined for pure phase particles may have little relevance to the kinetics of metal sorption in natural environments. In addition, natural waters can have complex solution speciation with much of the Ni, Cu and Zn in estuaries existing bound to organic ligands (Donat et. al., 1994; Sedlak et. al., 1997; and Kozelka and Bruland, 1998). From the work of Li et al., (1984); Nyffeler et al., (1984); Balistrieri and Murray, 1986; and Jannasch et al., (1988), there is experimental evidence that under natural conditions, dissolved/particulate metal partitioning can occur over longer time scales on the order of days to months. In these studies, metal radioisotopes were used to trace adsorption from dissolved to particulate forms in laboratory experiments using natural field samples.

Since natural aquatic systems are complex, one would ideally employ a method that could document this process directly and in-situ, with minimal disturbance from “ambient” conditions. This requires tracers that have little or no environmental consequences, ruling out radioactive isotopes commonly used to study natural processes within the confines of the laboratory. However, with the development of high resolution, inductively coupled plasma mass spectrometry (HR-ICPMS), naturally occurring, low abundance, stable isotopes can be used as tracers for such experiments. In this study, such isotopes of the metals Ni, Cu and Zn were added to estuarine waters and suspended sediments in laboratory bottle experiments. These low abundance isotope additions shift the isotopic ratios for each metal away from natural abundance ratios but still allow the sorption process to be studied close to “ambient” metal concentrations. This study verifies the potential for low abundance stable isotopes to be used as powerful environmental-tracers, while assessing sorption equilibrium and kinetic parameters between the...
estuarine waters and suspended particles of South San Francisco Bay. The study is valuable in part because of the novel approach employed to examine metal sorption partitioning, with its potential application to future in-situ studies using limno-corrals in natural aquatic systems. This study is also important because it uses estuarine seawater as a medium, while more of the existing literature on the subject has focused on sorption processes in fresh waters.

1.1 The Study Site: South San Francisco Bay Estuary.

The San Francisco Bay estuary is a contaminated coastal embayment with respect to Ni, Cu and Zn concentrations in both sediments and dissolved phases. In South San Francisco Bay, where this study is focused, both dissolved Ni and Cu concentrations can exceed EPA marine water quality criteria (Flegal et al., 1991; Fig. 1). “Over three billion dollars have been invested on waste water treatment facilities to improve the water quality of the estuary during the past three decades” (Flegal et al., 1996). Despite these efforts, high dissolved metal concentrations persist in the estuary, suggesting possible causal relationships between historically contaminated sediments and contemporary aqueous concentrations (e.g. South Bay concentrations of dissolved Ni and Cu as high as 70 nM in summer, with dissolved Zn as high as 20 nM in summer (Flegal et al., 1991).

In addition, San Francisco Bay is a shallow estuary, with an average depth of only 6 m (Fig. 1; Conomos, 1979). Large portions of the Bay are as shallow as 2 m, particularly in the South Bay, allowing wind-induced resuspension of contaminated bottom sediments to be a common, if not a daily occurrence, during summer (Krone, 1979; Conomos et al., 1985). High suspended solids concentrations resulting from these resuspension events tend to coincide with peak dissolved metal concentrations in South Bay, although there have been no studies to date
investigating any causal link between the two (data compared from Flegal et al., 1991, Flegal, 1993 and Schoellhamer, 1993).

In order to address the possibility of resuspended sediments acting as a source (and/or sink) for dissolved metal concentrations in the Bay, the kinetic time scales of sorption reactions must first be assessed. Knowing the kinetic time scales of metal sorption processes allows evaluation of the exchangeable particulate metal pool as an essentially inert or labile chemical form in the overall speciation of Ni, Cu, and Zn in the South Bay. The dynamics of sorption exchange between these chemical forms can then be evaluated within the context of other metal cycling processes occurring in the Bay. These time scales can also be compared to particle residence times in the water column during typical resuspension events, as well as to water mass residence times in the Bay. Overall, site-specific kinetic rate constants estimated here can also be used in numerical metal partitioning models to provide more rigorous evaluation of the fate and transport of metals injected into the Bay via waste and urban runoff processes.
2. BACKGROUND

Most existing environmental data on metal-particle associations in natural waters is expressed as the extent to which metals have different particle binding affinities, and is reported as a distribution coefficient, $K_D$. The term $K_D$ is an observational parameter based upon “snapshot” field measurements and is defined as the measured ratio of metal concentration on particles ($C_s$ in moles of exchangeable metal per kg dry sediment), to the concentration in water ($C_w$ in moles metal per L water):

$$K_D = \frac{C_s}{C_w} \quad [L \, kg^{-1}] \quad (1).$$

Another common way to write $K_D$ is:

$$K_D = \frac{[M_p]}{[M_d]}(C_p)^{-1} \quad [L \, kg^{-1}] \quad (2),$$

based on observed measurements of the exchangeable particulate metal concentration $[M_p]$ (moles per L, operationally defined here as that metal retained by a 0.4 µm membrane filter and subsequently leachable by 20% acetic acid), the dissolved metal concentration $[M_d]$ (moles per L), and the particle concentration ($C_p$) (kg particles per L). Note that $K_D$ is usually reported as an observed parameter. It is often unknown if a system is at equilibrium with respect to sorption processes, yet a true equilibrium $K_D$ value is only given if equilibrium dissolved and exchangeable particulate metal concentrations are used in the calculation.

Results of a South Bay, January 1994 sampling effort at the same sampling location as this study (Dumbarton Bridge station) report $K_D$ values for Ni, Cu and Zn of $10^{4.6}$, $10^{4.2}$ and $10^{4.8}$ L kg$^{-1}$, respectively (Sanudo-Wilhelmy et al., 1996). Mean observed $K_D$ values of $10^{4.7}$, $10^{4.3}$ and $10^{5.5}$ L kg$^{-1}$, for Ni, Cu and Zn in the South Bay were also calculated here using Flegal (1993) and (1995) Dumbarton Bridge station data (published in the San Francisco Estuary Institute...
Regional Monitoring Program for Trace Substances Annual Reports, SFEI-RMPTS). These data came from six sampling events taken in different seasons (three in each year), with measured particle concentrations that ranged from 3 mg/L to 72 mg/L. These mean $K_D$ values correspond to 57% of total Ni, 74% of total Cu and 30% of total Zn being in the dissolved phase in the South Bay in 1993 and 1995.

A simple sorption reaction reflecting this metal partitioning can relate kinetic rate constants to the distribution coefficient:

$$M_d + \text{particles} \xrightarrow{k_f} \xleftarrow{k_b} M_p$$  \hspace{1cm} (3).

Assuming the principle of microscopic reversibility and using equation 2 to calculate an equilibrium $K_D$, we now have

$$k_f \left(C_p\right) [M_d]_{eq} = k_b [M_p]_{eq}$$ \hspace{1cm} (4),

where $k_f$ is the forward adsorption rate constant for the reaction (equation 3) proceeding to the right, and $k_b$ is the backward desorption rate constant for the reaction mechanism proceeding to the left. $k_f$ is a second order rate constant with units of L (kg particles)$^{-1}$ (day)$^{-1}$ while $k_b$ is a first order rate constant with units of (day)$^{-1}$. The particle concentration ($C_p$) is measurable. For a given experiment dealing with an isolated sampling event, ($C_p$) can be treated as a constant. By incorporating ($C_p$) into the second order forward rate constant $k_f$, a new pseudo-first order forward rate constant $k'_f$ with units of (day)$^{-1}$ can be defined, and equation 4 can be simplified to:

$$k'_f [M_d]_{eq} = k_b [M_p]_{eq} \text{ where } k'_f = k_f(C_p)$$ \hspace{1cm} (5).

The ratio of the kinetic rate constants in equation 5 is thus equivalent to the product of the equilibrium $K_D$ and the particle concentration, according to equation 2.

Perturbations to the system, such as inputs of metals in dissolved or particulate form, will cause the variables $[M_d]$ and $[M_p]$ to change with time depending on whether net adsorption or
net desorption is occurring. Given enough time, the system will come to a new equilibrium. We can formulate a new transient non-equilibrium $K_D$ that will change over time such that

$$K_D(t) = \frac{[M_p]\text{t}}{[M_d]\text{t} - \[M_d\text{t}] (cp)^{-1}} \text{ where } K_D(t \to \infty) = K_{D_{eq}} \quad (6).$$

Fig. 2a depicts such a scenario, in which the dissolved metal concentration $[M_d]$ is suddenly increased at time zero. Net adsorption begins to occur, causing $[M_d]$ to drop and $[M_p]$ to increase. This process is countered by desorption and steady state is eventually reached where the two concentrations again become constant. Fig. 2b represents graphically the expected evolution of $K_D(t)$, with $(Cp)$ held constant. For a reversible first order reaction such as the sorption process assumed here, the characteristic reaction time “$\tau$” is equal to $(k_f' + k_b)^{-1}$. For times $<< \tau$, the reaction has not progressed significantly, while for times $\sim > 4\tau$ the reaction approaches completion and the system is near equilibrium (Morel and Herring, 1993).

The change in dissolved metal concentration with time can be expressed as:

$$\frac{d[M_d]}{dt} = -k_f'[M_d] + k_b[M_p] \quad (7).$$

While both dissolved and particulate metal concentrations can be measured in the laboratory, for studies using tracers that are added in dissolved form it is useful to rewrite the particulate metal isotope concentration as a function of the dissolved metal isotope concentration at time $t$:

$$[M_p] = [M_p]_0 + [M_d]_0 - [M_d] \quad (8).$$

Here $[M_p]_0$ and $[M_d]_0$ are measured values (the initial particulate and dissolved metal isotope concentrations when the system perturbation occurs). $[M_d]_0$ includes both the initial ambient dissolved concentration as well as the added amount (spike) of that metal isotope. The difference ($[M_d]_0 - [M_d]$) represents the lowering of the dissolved isotope concentration by adsorption onto the particulate phase at time $t$. Substituting equation 8 into equation 7 gives:
\[
\frac{d[M_d]}{dt} = -k'_f[M_d] + k_b ([M_p]_0 + [M_d]_0 - [M_d]) \tag{9}
\]

Integrating equation 9 yields a solution where only \(k'_f\) and \(k_b\) are left unknown:

\[
[M_d] = \frac{1}{(k'_f + k_b)} \left[ k_b[M_p]_0 \left( 1 - \exp^{-(k'_f + k_b)t} \right) + [M_d]_0 (k_b + k'_f \exp^{-(k'_f + k_b)t}) \right] \tag{10}
\]

Equation 10 can be used to fit experimentally generated time series of changing dissolved isotope concentrations to determine \(k'_f\) and \(k_b\). Note that from equation 10 the new equilibrium dissolved metal concentration following a perturbation can be expressed as:

\[
[M_d]_{eq} = \frac{k_b ([M_p]_0 + [M_d]_0)}{(k'_f + k_b)} \tag{11}
\]

This is the essential background summarizing our approach to the quantification of sorption kinetics. It is adapted from Nyffeler et al., (1984), in which time series of dissolved concentrations of metal radioisotopes were used to assess the kinetics of adsorption with natural particles. In our study, however, we also tracked the evolution of particulate metal concentrations. This allows both an assessment of mass balance and provides a second and independent data source for estimating kinetic constants. Substituting equation 10 into equation 8 gives an expression for the particulate metal concentration as a function of time that can be used to curve fit experimentally determined particulate time series data:

\[
[M_p] = [M_p]_0 + [M_d]_0 - \left[ \frac{1}{(k'_f + k_b)} \left[ k_b[M_p]_0 \left( 1 - \exp^{-(k'_f + k_b)t} \right) + [M_d]_0 (k_b + k'_f \exp^{-(k'_f + k_b)t}) \right] \right] \tag{12}
\]

In analogy with equation 11, the new equilibrium exchangeable particulate metal isotope concentration from equation 12 can be expressed as:

\[
[M_p]_{eq} = \frac{k'_f ([M_p]_0 + [M_d]_0)}{(k'_f + k_b)} \tag{13}
\]
3. EXPERIMENTAL

3.1 Sampling Procedures

In conjunction with the summer 1997 sampling effort for the Regional Monitoring Program for Trace Substances (RMPTS) in San Francisco Bay (A.R. Flegal, P.I.), a 20-L acid washed carboy was filled with unfiltered water from the South Bay, just north of the Dumbarton Bridge (monitoring station BA30). Simultaneously, three acid washed 2.5-L polycarbonate bottles were filled with 2 L 0.45 µm cartridge-filtered water to be used as particle free controls in the adsorption experiment. An additional L of 0.45 µm cartridge-filtered water was also taken and acidified, and 0.5 L of unfiltered water was taken and acidified. These acidified samples were used to determine ambient metal concentrations prior to spike additions in the adsorption experiments. All unacidified samples were stored in a cooler and immediately brought back to the lab.

The same day, the 20-L carboy was homogenized using a Teflon coated propeller blade and shaft attached to a motor on the outside of the carboy cap. Eight 2.5-L acid washed polycarbonate bottles were rinsed with a portion of this well mixed water-sediment suspension, and then filled to pre-measured 2-L volume lines. Four of the eight 2.5-L unfiltered bottles were then placed in black plastic bags to protect from light exposure and put on a shaker table to keep the sediment in suspension. The four remaining 2.5-L unfiltered bottles were then individually microwaved using the high setting on a conventional Quasar microwave oven. They were microwaved in 2 minute increments for a total of 14 minutes per bottle to sterilize the samples in an attempt to control for microbial growth effects on adsorption (Keller et al., 1988). Once the microwaved bottles cooled they were also placed in black plastic bags and then put on the shaker table. The three control bottles containing 0.45 µm cartridge-filtered Bay water were also placed in black plastic bags on the shaker table. The total of eleven 2.5-L experimental bottles were then kept at constant temperature (24°C) in bags on the oscillating shaker table at all times during the two week experiment, except for when removal was necessary for filtration sampling.
3.2 Low Abundance Stable Isotope Spike Additions

Prior to spike additions, a trace metal clean, in-line duo-filtration system was set up in a clean hood. This system allows direct filtration of 100 ml subsamples out of the larger experimental bottles, providing “snap shot” samples where “dissolved” metals are separated from operationally defined “particulate” metals at set times during the experiment. 0.4µm pore size filter membranes (Poretics brand) that had been previously soaked in 3 N HCl acid overnight and then rinsed with MilliQ water were used in the filtration apparatus. Within 24 hours of sampling from the South Bay, additions of selected low natural abundance, stable isotopes of Ni, Cu and Zn were made to each experiment bottle, marking the “time zero” point in the two week adsorption experiment. To each of the eleven 2.5-L bottles on the shaker table 500 µl of 85.2 µmol ⁶¹Ni/kg, 500 µl of 144.4 µmol ⁶⁵Cu/kg and 250 µl of 95.3 µmol ⁶⁸Zn/kg were added. These stock solutions were separately analyzed using HR-ICPMS, to check for isotope impurities. This corresponds to concentration additions of 21 nM ⁶¹Ni, 2 nM ⁶⁰Ni, 2 nM ⁵⁸Ni; 36 nM ⁶⁵Cu, 0.11 nM ⁶³Cu; 12 nM ⁶⁸Zn, and 0.25 nM ⁶⁴Zn. Spikes were added to two bottles at a time, which were then immediately shaken and placed on the duo-filtration rig to obtain the first set of post-spike filtration samples. This process took roughly 20 minutes between each set of bottles. 100 ml filtration samples were then taken after 8 hours and then at 1, 3, 6, 10 and 14 day intervals. Experiment bottles were sampled following the same sequence each time so that the filtration sample times were correct within 20 minutes. For each sample taken, the filtrate was filtered directly into 125 ml acid cleaned polyethylene bottles, acidified with 400 µl of 6 N QHCl and stored double bagged. The filter membranes were placed in acid cleaned 7 ml high-density poly-ethylene vials, double bagged and frozen for later analyses.

3.3 Determination of Trace Metal Concentrations

Trace metal concentrations for both dissolved and particulate samples were determined using HR-ICPMS. A method was developed that employs a combination of medium and low resolution mass spectrometry, counting and analog mode detection, and uses In, Ga and Rh as internal standards. A suite of metal isotopes were analyzed, including the stable isotopes of Cu, Ni, Zn, Fe, Mn, Co, Pb, Ag, and Cd.
Mixed calibration standards were used, having the appropriate matching acid matrix as the final samples analyzed from both dissolved and particulate procedures.

Prior to analysis on HR-ICPMS, the dissolved samples required a pre-concentration step, which was accomplished using a multiple-ligand sequential extraction technique. This pre-concentration step also served to isolate the metals of interest from the original seawater matrix to an acid matrix ideal for subsequent analysis with HR-ICPMS. The technique was developed for this study from a synthesis of various procedures outlined in (Danielsson et al., 1978; Bruland et al., 1979; Landing and Bruland, 1980; Bruland et al., 1985; Batterham and Parry, 1996). Here, a 100 ml filtered, acidified sample of Bay water is transferred to a Teflon separatory funnel. The sample is buffered at pH 4.3 with 400 µl of QNH$_4$-Acetate. 500 µl of a 1% solution of each of the ligands 1-pyrrolidinedithiocarbamate (PDC) and diethyldithiocarbamate (DDC) are then added to chelate dissolved Cu, Ni, Zn, Fe, Co, Pb, Ag, and Cd in the Bay water sample. The metal-dithiocarbamate complexes that form are neutrally charged and hydrophobic and thus, extract into chloroform. To extract the metals, 7 ml of chloroform is added and the funnel shaken vigorously for 5 minutes. The two phases are then allowed to separate for 5 minutes. As the chloroform solution containing the metal-ligand complexes is denser than the aqueous phase, it can be drained off into a trace metal clean polyethylene bottle suitable for use in the HR-ICPMS auto-sampler.

Following the first extraction, the sample pH is adjusted to 9.3 with 500 µl of QNH$_4$-OH. Then a second extraction is performed by adding the ligand 8-hydroxyquinoline (oxine) already dissolved in a chloroform solution to bind dissolved Mn and residuals of the other metals not extracted in the first step. Here 6 ml of 0.1% oxine in chloroform is added to the same 100 ml sample of Bay water. The funnel is again vigorously shaken for 5 minutes and the phases are allowed to separate for another 5 minutes. Then the second chloroform solution containing the oxine-metal complexes is drained from the funnel and combined with the first chloroform extraction. Together they are acidified with 200 µl of concentrated nitric acid, evaporated overnight in a laminar flow trace metal clean hood, and then taken up in 5 ml of a stock 0.5 N nitric acid solution containing the internal standards In, Ga and Rh. This procedure results in
a 20-fold concentration of the original sample metal levels into a matrix suitable for ICPMS. It also simultaneously removes the bulk of the major seawater salts that can build up on the torch of the ICPMS as well as produce potential isotope interferences upon analysis.

This method was verified to be quantitative and reproducible using metal radioisotope additions to South Bay water samples. Means and standard deviations for the total extraction percent recoveries of each metal tested are: 95.3% ± 1.8% (n=4) for $^{109}$Cd, 94.3% ± 2.1% (n=3) for $^{57}$Co, 93.7% ± 1.5% (n=4) for $^{59}$Fe, 94.1% ± 1.8% (n=4) for $^{65}$Zn and 91.3% ± 0.8% (n=4) for $^{54}$Mn. These total extraction percent recoveries derived in the radioisotope lab were taken into account for each stable metal isotope analyzed using HR-ICPMS. The accuracy of the method was tested by extracting samples of Canadian National Research Council certified reference nearshore seawater (CASS-3) at the same time as filtrates from the adsorption experiment. Results from these CASS-3 organic extractions are compared to the certified concentrations in Table 1. Organic extraction results for Co, Fe, Mn, Ni and Zn are within the reported 95% confidence limits of the certified concentrations. The value we obtained for Cu was 18% higher than the certified value and falls just outside the reported 95% confidence limit.

The exchangeable particulate metal pool was assessed using a 20% acetic acid leach, adapted from Landing and Bruland (1987). The frozen filter membranes were transferred to acid cleaned centrifuge tubes and allowed to defrost. 7 ml of 20% HAc containing 50 ng/g of the internal standards In, Ga and Rh were added to each tube and shaken. The samples were kept at room temperature for two hours and then centrifuged at an effective g-force of 1600 for 5 minutes. The supernate was decanted back into the acid cleaned sample vials and 25 µl of concentrated nitric acid was added to each acetic acid leachate. During earlier method development investigations, considerable signal drift on the ICPMS was observed when running straight 20% acetic acid standards. However, this drift was removed if a small amount of nitric acid was added to the standards, stabilizing the signal and allowing direct analysis of metals in the carbon rich acetic acid matrix without requiring further wet chemistry manipulations.
3.4 Particle Concentrations

Particle concentrations for each of the eight unfiltered experimental bottles were determined by pre-weighing 47 mm diameter, 0.4 μm pore size Poretics polycarbonate filter membranes, filtering known volumes from each well mixed bottle and then drying the membranes in a Precision Thelco oven at 68°C overnight. Membranes were placed in a dessicator for half an hour to cool prior to reweighing. The mean particle concentration for the eight unfiltered bottles was 34.5 ± 1.4 mg/L Bay water (n=8). The particle concentration determined with the 0.4 μm pore size Poretics filters on the 0.45 μm cartridge-filtered control bottles was found to be 0.9 ± 0.1 mg/L water (n=4), suggesting that there was a small amount of particles in the size class between 0.4 and 0.45 μm.
4. RESULTS

For the metals Ni, Cu and Zn, three sets of data were generated. These included dissolved and exchangeable particulate concentrations as a function of time, graphs of changing isotopic ratios as a function of time, and curve-fits of mean dissolved and exchangeable particulate isotopic concentrations as a function of time, which were used to extrapolate kinetic rate constants. Of the three elements studied, the Ni data set displays all of the following: mass balance between the observed loss of $^{61}$Ni from the dissolved pool and the resulting increase in exchangeable particulate $^{61}$Ni over time, the data converge to a predicted isotopic equilibrium ratio, and the curve-fits of the separately generated dissolved and exchangeable particulate $^{61}$Ni data give matching results for both forward and backward modeled kinetic rate constants.

4.1 Nickel Concentration and Isotopic Ratio Results

Prior to spike addition, “initial ambient” dissolved metal concentrations were measured from replicate sub-samples of the 0.45 µm cartridge-filtered and acidified South Bay water. For Ni, the mean total dissolved concentration was 56.0 ± 1.5 nM (n=6). The initial ambient acetic acid leachable (exchangeable) particulate Ni had an average value of 8.7 nM. Thus, at the start of the experiment the Ni was predominantly dissolved, with only 13.4% occurring as exchangeable particulate Ni. Using the mean particle concentration from the experiment bottles of 34.5 ± 1.4 mg L$^{-1}$ (n=8), an initial ambient Ni $K_D$ of 10$^{3.65}$ L kg$^{-1}$ can be calculated (Table 2).

This initial ambient $K_D$ value is nearly an order of magnitude lower than the mean Ni $K_D$ value calculated using the South San Francisco Bay monitoring data from 1993 and 1995, presented in the background section (Flegal, 1993 and 1995). Both seasonal and particle concentration effects are likely to be involved in this difference but it should also be noted that different methods were used to estimate the exchangeable particulate metal fraction. Here, filter membranes containing Bay particles were exposed to a 20% acetic acid leach (pH = 2) for two hours to measure the exchangeable particulate metal pool. Under the regional monitoring program
protocols, “total dissolvable metal concentrations” (unfiltered samples acidified to pH ~ 1.8 with hydrochloric acid and stored for a minimum of a month prior to analysis) and “dissolved metal concentrations” (filtered samples acidified to pH ~ 1.8) are measured. The leachable particulate metal is then estimated as the difference between the measured dissolved and total dissolvable concentrations. (Flegal, 1993).

The dissolved Ni data from the time series sorption experiment for the unmicrowaved samples are presented in Fig. 3a. Each data point in the time series represents an isotope concentration determined from separate bottle experiment replicates. Mean “initial ambient” concentrations for the individual Ni isotopes measured prior to spike addition are indicated above the asterisk at the left side of Fig. 3a. These measured isotope concentrations were compared (as percentages of the measured total ambient Ni concentration) to expected natural abundance percentages and agreed to within 1%. The isotope chosen to trace Ni adsorption in the experiment was $^{61}$Ni, which under natural abundance occurs at 1.13% (the measured $^{61}$Ni initial ambient abundance percentage determined for South Bay was 1.2%).

A 21 nM addition of dissolved $^{61}$Ni was made just prior to filtering the first set of samples. 2 nM of both $^{58}$Ni and $^{60}$Ni were also added along with the 21 nM $^{61}$Ni due to a slight Ni isotope impurity in the $^{61}$Ni spike, giving a predicted “time zero” total dissolved Ni concentration of 81 nM. The $^{61}$Ni addition altered natural abundance causing $^{61}$Ni to become the second most abundant Ni isotope in the bottle experiments. In the first filtration samples taken just after spiking, the $^{61}$Ni accounts for 28.4% of the total dissolved Ni concentration (up from 1.2%). Dissolved $^{61}$Ni concentrations are highest in the first filtration samples (average of 23 nM) and decrease with time, reaching a concentration of 18.5 nM after 14 days. Results from the microwaved 14-day sample are included in Fig. 3a to show that there was good agreement between the dissolved isotope concentrations determined for microwaved and unmicrowaved experimental bottles.

The ~ 4.5 nM decrease in $^{61}$Ni dissolved concentrations seen over the 14-day period was reflected in a 3.6 nM increase in exchangeable particulate $^{61}$Ni concentrations in both unmicrowaved and microwaved bottle experiment replicates (Fig. 3b-c). $^{61}$Ni in the exchangeable
particulate fraction already started to increase in the first samples taken after the spike addition was made, while natural abundance would predict $^{61}\text{Ni}$ to be about a third of what is observed. There was a 20-minute lag between metal spike additions and completion of the first set of filtration samples. Together these suggest that a small amount of the added dissolved $^{61}\text{Ni}$ had already become adsorbed to particle surfaces by the time the first “$t = 20$ minute” samples were filtered. Results from microwaved replicates indicate a similar pattern (Fig. 3c).

The perturbation to the system occurred by increasing the dissolved Ni fraction from 86.6% to 90.3% by $t = 20$ minutes just following the spike addition (Table 2). By day 14 the dissolved Ni fraction dropped back to 80.4% of the day 14 total (Fig. 3a-c). These results are reported as distribution coefficients ($K_D$) in Table 2. As expected, due to the dissolved addition, the $t = 20$ minutes $K_D$ fell from the ambient value of $10^{3.65}$ to $10^{3.49}$ L kg$^{-1}$. By day 14 it had increased to slightly higher than the original ambient partitioning with a $K_D$ of $10^{3.85}$ L kg$^{-1}$.

These data can also be presented as changing isotopic ratios with time. There was a modest decrease in the dissolved $^{61}\text{Ni}/^{60}\text{Ni}$ concentration ratio and a dramatic increase in the exchangeable particulate $^{61}\text{Ni}/^{60}\text{Ni}$ concentration ratio (Fig. 3d and 3e). Due to the predominance of the dissolved pool in South Bay Ni partitioning (see Table 2), the small exchangeable particulate $^{61}\text{Ni}/^{60}\text{Ni}$ ratio was much more sensitive to the $^{61}\text{Ni}$ spike addition (Fig. 3e). The 4.5 nM $^{61}\text{Ni}$ loss seen in the dissolved data was only 5.5% of the total dissolved Ni measured just after the spike addition, while the 3.6 nM $^{61}\text{Ni}$ increase seen in the exchangeable particulate data raised the total particulate Ni concentration measured just after the spike addition by 40%.

Predicted equilibrium ratios were also calculated for each metal isotope addition made. Tallying a budget that includes the initial dissolved, exchangeable particulate and added isotope concentrations for each isotope in the ratio and then dividing appropriately gives a theoretical predicted equilibrium ratio for the Ni sorption experiment:

$$\frac{([\text{Diss}^{61}\text{Ni}], + [\text{Particulate}^{61}\text{Ni}], + [\text{Added}^{61}\text{Ni}])}{([\text{Diss}^{60}\text{Ni}], + [\text{Particulate}^{60}\text{Ni}], + [\text{Added}^{60}\text{Ni}])} = \text{Predicted Equilibrium Ratio}$$

(14).
For $^{61}\text{Ni} / ^{60}\text{Ni}$, this resulted in a predicted equilibrium ratio of 1.1, which both the dissolved and exchangeable particulate ratio data converge to from different directions (Fig. 3d-e). By day 14, the mean exchangeable particulate $^{61}\text{Ni} / ^{60}\text{Ni}$ ratio data had climbed 89% of the way from the 0.04 natural abundance ratio to the 1.1 predicted equilibrium ratio.

### 4.2 Nickel Kinetic Rate Constant Determinations

With the assumption that the sorption processes are reversible, rate constants were estimated by curve-fitting the experimentally derived data as outlined in the background section. The dissolved $^{61}\text{Ni}$ concentration data were modeled using equation 10, and are presented in Fig. 4a. A forward rate constant $k'_f$ of 0.038 d$^{-1}$ and a backward rate constant $k_b$ of 0.13 d$^{-1}$ were estimated. A close match was found for the backward rate constant when the exchangeable particulate $^{61}\text{Ni}$ data were separately modeled using equation 12 (Fig. 4b). The forward rate constant estimate that resulted from the exchangeable particulate curve-fit was a $k'_f$ of 0.026 d$^{-1}$. Both the $k'_f$ and $k_b$ values from the two independent data sets match within the curve-fit error, with each curve representing 96-97% of the variance in each data set. The characteristic time of the sorption reaction based on these results is 6 days, and at $4\tau$ or on the order of 25 days, the reaction should have approached equilibrium (Table 3a). These results concur with the previously discussed laboratory findings that the exchangeable particulate $^{61}\text{Ni} / ^{60}\text{Ni}$ concentration ratios were within 89% of the predicted equilibrium ratio after two weeks.

### 4.3 Copper Concentration and Isotopic Ratio Results

The mean total initial ambient dissolved Cu concentration was $58.3 \pm 1.2$ nM (n=6). The initial ambient total acetic acid leachable particulate Cu concentration had an average value of 15.3 nM. Thus, at the start of the experiment the Cu was predominantly dissolved, with 20.8% occurring as exchangeable particulate Cu. Using these initial concentrations and the mean particle concentration, an initial ambient Cu $K_D$ of $10^{3.88}$ L kg$^{-1}$ can be calculated (Table 2). This initial ambient $K_D$ is within the range of $K_D$ values calculated from the South San Francisco Bay.
monitoring data (Flegal, 1993 and 1995), although on the lower end (mean $K_D$ for the six samplings in the two years of $10^{4.3}$ L kg$^{-1}$ for Cu).

The dissolved Cu isotope concentration data for the unmicrowaved samples are presented in Fig. 5a. $^{65}\text{Cu}$ was used as the Cu spike isotope, which at natural abundance accounts for 30.8% of total Cu (initial ambient abundance measured for South Bay was 31.3%). For this element, only two stable isotopes exist, neither one occurring at very low abundance percentages under natural conditions. Thus 36 nM $^{65}\text{Cu}$ was added in order to bring the dissolved $^{65}\text{Cu}$ concentration within the range of ambient dissolved $^{63}\text{Cu}$. As a result of this spike addition, total dissolved Cu concentrations were increased by 62%, with dissolved $^{65}\text{Cu}$ concentrations remaining slightly higher than $^{63}\text{Cu}$ concentrations throughout the two-week experiment. Dissolved $^{65}\text{Cu}$ in the $t = 20$ minute samples accounts for 53.9% of the total dissolved Cu measured, (up from the 31.3% measured prior to spiking).

The addition of 36 nM dissolved $^{65}\text{Cu}$ to the ambient $^{65}\text{Cu}$ concentrations measured gives a predicted concentration of 54.3 nM $^{65}\text{Cu}$ for the beginning of the experiment. However, the first post-spike dissolved $^{65}\text{Cu}$ concentrations measured were lower by 5.5 nM. This suggests a rapid removal process active in the 20-minute time interval between adding the isotope spikes and completing the first set of filtration samples. The dissolved $^{65}\text{Cu}$ concentrations continued to show a rapid decrease of ~ 8 nM in the first 24 hours of the experiment, followed by a steady decline over the remaining time examined, summing to a total of 15 nM loss of $^{65}\text{Cu}$ from the predicted 54.3 nM dissolved pool immediately after the spike addition. The dissolved $^{63}\text{Cu}$ concentration data showed a similar although less dramatic pattern, as only 0.11 nM $^{63}\text{Cu}$ was added along with the 36 nM $^{65}\text{Cu}$ due to a slight isotope impurity in the spike used. There was good agreement between samples taken from different replicate and microwaved control bottle experiments (only one data point appearing per sample time represents two overlapping and matching results).

The exchangeable particulate Cu data are presented in Fig. 5b. In the first filtration sample in the time series, $^{63}\text{Cu}$ was still the more abundant Cu isotope in the exchangeable particulate fraction. By 8 hours, however, the $^{65}\text{Cu}$ exchangeable particulate concentrations were higher than
for $^{63}\text{Cu}$. Both Cu exchangeable particulate isotope concentrations continued to climb as time proceeded, although the increase again was less dramatic for $^{63}\text{Cu}$. There was a 16 nM increase in exchangeable particulate $^{65}\text{Cu}$ concentrations over the course of the experiment, in good agreement with the 15 nM decrease seen in the dissolved $^{65}\text{Cu}$ data. The exchangeable particulate $^{63}\text{Cu}$ increased by 6.5 nM over the two weeks, matching closely the 6.3 nM decrease seen in the dissolved $^{65}\text{Cu}$ concentrations over this time. Thus there is a mass balance for both Cu isotopes in the two pools studied. The increase in exchangeable particulate concentrations and decrease in dissolved concentrations for both stable Cu isotopes indicate that net adsorption proceeded for total Cu since the time of the $^{65}\text{Cu}$ spike addition throughout the two-week experiment (Fig. 5a-b).

The 36 nM dissolved $^{65}\text{Cu}$ addition shifted the ambient Cu partitioning from 79.2% to 82.4% dissolved at t = 20 minutes. By the end of the two-week period the total dissolved Cu fraction had fallen below ambient levels to 64% dissolved (Table 2). As expected due to the dissolved addition, the t = 20 minutes $K_D$ dropped from the ambient value of $10^{3.88}$ to $10^{3.79}$ L kg$^{-1}$. By day 14 it was higher than ambient partitioning with a $K_D$ of $10^{4.21}$ L kg$^{-1}$. The exchangeable particulate $^{65}\text{Cu}$ concentration measured in the t = 20 minute samples represents about 15% of the total $^{65}\text{Cu}$ measured at that time in the bottle experiments, whereas by the end of the two weeks, the particulate $^{65}\text{Cu}$ pool had increased to about 39% of the total $^{65}\text{Cu}$ measured.

The dissolved Cu data are presented as isotopic concentration ratios in Fig. 5c. We expected the dissolved ratios to decline and approach the predicted equilibrium ratio from above, as was seen in the dissolved Ni data (Fig. 3d). However, most of the post-spike ratio data hover at or below the predicted equilibrium ratio of 1.16 for $^{65}\text{Cu} / ^{63}\text{Cu}$ (calculated according to equation 14, section 4.1). There is only a slight decline with time in the earliest time series data. When the predicted isotopic ratio of 1.35 calculated for conditions immediately after the spike addition are included in Fig. 5c (closed square), the decline is more evident, indicating that a significant part of the dissolved $^{65}\text{Cu}$ removal process had to have occurred in the first 20 minutes of the experiment.

The exchangeable particulate Cu isotopic ratio data also indicate that rapid adsorption occurred early on in the experiment, especially of the $^{65}\text{Cu}$ spike (Fig. 5d-e). At t = 20 minutes the
ratio was already halfway between the natural abundance ratio of 0.45 and the predicted equilibrium ratio of 1.16. The microwaved data showed a similar pattern (Fig. 5e). For the bulk of the experiment, the $^{65}\text{Cu} / ^{63}\text{Cu}$ isotopic ratio in the particulate pool was at or above the predicted equilibrium ratio. Together Fig. 5a-e indicate that the $^{65}\text{Cu}$ spike addition drove net Cu adsorption, with a mechanism whereby the added $^{65}\text{Cu}$ was preferentially removed to the particulate phase over ambient $^{63}\text{Cu}$.

### 4.4 Copper Kinetic Rate Constant Determinations

Curve-fits and corresponding kinetic rate constants extrapolated from both the dissolved and exchangeable particulate data are presented in Fig. 6a-b (solid curves) and the first two columns of the tables embedded in Fig. 6. For both sets of data, these initial fits were not as close-fitting as those found for the $^{61}\text{Ni}$ data. While the best fits still represent between 89-90% of the variance seen in each data set, the two pairs of rate constant estimates do not match within the error of the curve-fits. As the rate constants are not well constrained, a second set of curve-fits were generated from the Cu data excluding the t = 20 minutes data and beginning with t = 8 hours (dashed curves). Reasoning for this reinterpretation of the data is developed in the discussion section 5.2. The results of this second set of fits (given in the last two columns of the tables in Fig. 6) show smaller rate constant solutions with higher $R^2$ values for both the dissolved and particulate Cu data sets. An estimate for $k'_f$ and $k_b$ of 0.07 d$^{-1}$ and 0.12 d$^{-1}$ respectively can be made for Cu by averaging the solutions found for the dissolved and particulate data, excluding the t = 20 minutes data. These rate constant estimates suggest a characteristic reaction time of 5 days for Cu with respect to metal sorption exchange in the water column of South Bay (Table 3b).
4.5 Zinc Concentration and Isotopic Ratio Results

The mean total dissolved Zn concentration was 13.5 ± 0.3 nM (n=6). The initial ambient total acetic acid leachable particulate Zn had an average value of 15.5 nM. Thus, at the start of the experiment the ambient Zn was roughly equally split between the dissolved and particulate fractions. Using these initial concentrations and the mean particle concentration, an initial ambient Zn $K_D$ of $10^{4.52} \text{ L kg}^{-1}$ can be calculated (Table 2). This initial ambient $K_D$ value is within the range of $K_D$ values calculated from the San Francisco Bay monitoring data (Flegal, 1993 and 1995), although on the lower end (mean $K_D$ of $10^{5.55} \text{ L kg}^{-1}$ for Zn based on six samplings in two years).

Initial ambient dissolved concentrations prior to spiking were determined for the four major stable isotopes of Zn (Fig. 7a). The natural isotopic abundance of $^{68}$Zn is 18.8%, compared to 17.7% measured in the ambient South Bay water. 12 nM of $^{68}$Zn was added as the dissolved Zn spike, which included a 0.25 nM addition of $^{64}$Zn as well. As a result of this spike addition, $^{68}$Zn became the dominant Zn isotope throughout the course of the bottle experiments. In the t = 20 minutes samples, $^{68}$Zn accounted for 54.4% of the total dissolved Zn (up from the measured ambient abundance of 17.7%). $^{68}$Zn concentrations dropped rapidly in the first 8 hours of the experiment and then decreased steadily, approaching dissolved $^{64}$Zn concentrations. A total dissolved $^{68}$Zn loss of 5.3 nM occurred through day 10 of the experiment. There was good agreement between samples from different bottle experiment replicates, with the exception of samples from day 14. These day 14 data were omitted from Fig. 7a and 7c due to obvious Zn contamination in these dissolved samples (obvious as the elevated concentrations occurred according to natural abundance and not according to the adjusted experiment isotopic ratios).

The unmicrowaved exchangeable particulate Zn data are presented in Fig. 7b. Initially the exchangeable particulate $^{68}$Zn concentration was below that of $^{66}$Zn but by 8 hours had exceeded it and continued to increase with time. Over the course of the experiment there was an observed 3.7 nM increase in the exchangeable particulate $^{68}$Zn from ambient levels, low compared to the 5.3 nM drop seen in the dissolved $^{68}$Zn concentrations (Fig. 7a). However, when mass balance for total Zn is considered, a closer match was found. The total Zn dissolved data showed a 6.3 nM decrease.
with a corresponding 6.1 nM increase in the total exchangeable particulate Zn up from ambient levels.

The 12 nM dissolved $^{68}$Zn addition caused the total Zn partitioning to shift from 46.7% to 59.2% dissolved in the t=20 minute samples. The total dissolved Zn fraction dropped back to 44.9% by the end of the experiment (Table 2). Due to the $^{68}$Zn addition occurring in the dissolved form, the t=20 minutes $K_D$ fell from the ambient $K_D$ of $10^{4.52}$ to $10^{4.30}$ L kg$^{-1}$. By the end of the experiment the $K_D$ returned to close to the ambient value ($10^{4.55}$ L kg$^{-1}$).

The dissolved concentration data are plotted as isotope ratios in Fig. 7c. The dissolved $^{66}$Zn/$^{64}$Zn and $^{67}$Zn/$^{64}$Zn ratios showed little change with time compared to $^{68}$Zn/$^{64}$Zn. The change in slope of dissolved $^{68}$Zn/$^{64}$Zn with time showed a break at 8 hours, became much more gradual by day 1 in the experiment and converged towards the predicted equilibrium ratio of 1.14 (calculated according to equation 14, section 4.1). As in the dissolved Zn ratio data (Fig. 7c), the exchangeable particulate $^{66}$Zn/$^{64}$Zn and $^{67}$Zn/$^{64}$Zn ratios changed only slightly with time (Fig. 7d). Although the exchangeable particulate $^{68}$Zn/$^{64}$Zn climbed slightly with time it did not reach the 1.14 predicted equilibrium ratio by day 14.

### 4.6 Zinc Kinetic Rate Constant Determinations

The curve-fit for all the exchangeable particulate $^{68}$Zn data is presented in Fig. 8b (solid curve). This solution accounts for 95% of the variance seen in the data and estimates $k'_f$ as 0.22 d$^{-1}$ and $k_b$ as 0.39 d$^{-1}$. The curve-fit for all the dissolved $^{68}$Zn data showed more variance, with an $R^2$ value of 0.86 (solid curve, Fig. 8a). The $k_b$ estimates from both data sets matched almost exactly while the $k'_f$ estimates matched within the margins of error associated with both curve-fits. Curve-fits excluding the t = 20 minutes data and beginning with the t = 8 hours data were also generated for Zn (dashed curves with results in the last two columns of tables in Fig. 8), the interpretations of which are discussed in section 5.2. This second set of curve-fits finds smaller rate constant solutions, giving a slower characteristic reaction time of 4 days calculated using an average of these new rate constants (Table 3b).
5. DISCUSSION

5.1 Isotope Ratio Results and Dissolved Speciation Considerations.

Examining the isotopic ratio data of the three metals investigated reveals different responses to the sorption experiment. The Ni experiment proved to be the most successful, with both the dissolved and exchangeable particulate Ni isotopic ratio data converging towards the predicted equilibrium ratio with mass balance (Fig. 3d-e). The isotopic ratio data of both Cu and Zn deviated from this expected pattern in different ways, and can be interpreted in light of available dissolved metal speciation data for South Bay.

For Cu, the nearly constant isotopic ratios seen in the dissolved data at the predicted equilibrium value from day 1 of the experiment suggest rapid removal of the added $^{65}$Cu from the dissolved phase (Fig. 5c). This is reflected in the roughly four times faster kinetic rate constants determined from the initial Cu curve-fits (solid curves, Fig. 6), compared to Ni. The high $^{65}$Cu/$^{63}$Cu exchangeable particulate ratios suggest that the added $^{65}$Cu was more readily adsorbed to particle surfaces than the ambient Cu, particularly at the very beginning of the experiment (Fig. 5d-e). These results can be explained by considering the different chemical forms in which the ambient and added dissolved Cu exists at the time the experiment begins.

The Cu isotope spike is added in a matrix of Milli-Q water acidified with nitric acid, and so is present as dissolved inorganic species prior to being mixed with the Bay water samples. Upon addition to the estuarine water, the inorganic $^{65}$Cu spike should equilibrate essentially instantaneously with the inorganic, dissolved ambient Cu, here defined as [Cu'] (the sum total of hydrated free Cu$^{2+}$ and inorganically complexed Cu). Given the salinity and pH conditions of South Bay, 90-95% of ambient [Cu'] should be inorganically complexed Cu, (CuCO$_3$ being the dominant species), with 5-10% as free Cu (Donat et al., 1994). However, studies present
evidence that naturally occurring Cu-chelating organic ligands exist in South Bay, dominating dissolved Cu speciation (80-92% of total dissolved Cu being strongly complexed with organic ligands, here defined as CuL₁, Donat et al., 1994). More recent data indicates that > 99% of Cu in South Bay is organically complexed, with a slight excess of strong Cu-binding ligands (Beck et al., 2002). The increase of total dissolved Cu from ~58 nM to ~94 nM in this study would have titrated this excess ligand, leaving some portion of the $^{65}$Cu addition as Cu′ rather than as CuL₁. Under “ambient Bay conditions,” both the ambient $^{65}$Cu and the ambient $^{63}$Cu are strongly complexed with organic ligands. We suspect that the rapid decrease in the first 24 hours of the experiment of ~7-8 nM dissolved Cu$^{65}$ (Fig. 5a) was due to the added Cu$^{65}$ not being equilibrated with the Cu bound to organic ligands, resulting in the preferential removal of Cu$^{65}$ as Cu′ from the dissolved phase.

The exchangeable particulate Cu isotopic data (Fig. 5d-e) also suggest that a portion of the added inorganic $^{65}$Cu equilibrated with the suspended particle surface sites more quickly than with the naturally occurring CuL complexes present in the Bay water samples. If the kinetics of Cu′ sorption to particles were significantly more rapid than the kinetics of exchange with the Cu bound to various Cu-binding organic ligands, such an observed favored adsorption of the added inorganic $^{65}$Cu would result. To date, the kinetics of Cu binding by such naturally occurring organic ligands remains unquantified. However, from the speciation work of Donat et al., 1994, the binding strengths of these South Bay Cu binding organic ligands have been measured. Conditional stability constants (with respect to Cu$^{2+}$) were found to be on the order of $10^{13.5}$ M⁻¹ for the class of strong Cu-binding organic ligands. Such strong binding constants infer slow dissociation rates and suggest that the added $^{65}$Cu did not adequately equilibrate with the organically chelated Cu, allowing the Cu$^{65}$ tracer to become preferentially sequestered into
particulate form. To test this interpretation, in future experiments it would be ideal to add the Cu tracer in a form identical to ambient Cu, by somehow pre-equilibrating it with filtered South Bay water containing an excess of natural organic ligands.

For Zn, the dissolved $^{68}\text{Zn}/^{64}\text{Zn}$ isotope ratios fall towards the calculated predicted equilibrium ratio by day 10 of the experiment, as expected (Fig. 7c). However, the exchangeable particulate $^{68}\text{Zn}/^{64}\text{Zn}$ isotope data climb just 40% of the way to the predicted equilibrium value by day 10 (Fig. 7d-e). Of the metals examined here, Zn was the only one where the ambient particulate fraction was larger than the dissolved fraction (53% particulate, Table 2). Consider that if the 20% acetic acid used here leaches more than the readily exchangeable fraction from the particles, then that portion of metal removed beyond the exchangeable particulate fraction should be comprised of isotope concentrations according to natural abundance isotope percentages. Here, this would mean more of the high abundance isotope $^{64}\text{Zn}$ and less of the low abundance isotope $^{68}\text{Zn}$ being extracted from the particulate samples than expected according to the predicted equilibrium ratio following the spike addition. This would dampen the increase in particulate $^{68}\text{Zn}/^{64}\text{Zn}$ concentration ratios over time, as seen in Fig. 7d-e. It is possible that this process is controlling the data for Zn without having a significant effect on the Cu or Ni particulate isotope ratio results because these latter two metals occur predominantly as dissolved species in South Bay. These results call for further investigations that rigorously define and verify the exchangeable particulate fraction experimentally. However, these results also illustrate that the low occurrence stable isotope tracing technique used here would lend itself well to such an investigation. Predicted equilibrium isotope ratios could be used as criterion for evaluating the effectiveness of a suite of different leaching techniques at stripping off only the readily exchangeable particulate metal fraction.
5.2 Alternate Interpretation of Copper and Zinc Kinetic Results.

The rapid draw down of dissolved $^{65}$Cu in the first 8-24 hours of the experiment may be the result of the added $^{65}$Cu initially occurring as Cu′ and being preferentially removed to the exchangeable particulate phase relative to the ambient chelated Cu. As Cu has no truly low abundance stable isotope, a large addition of 36 nM of $^{65}$Cu was used to bring the dissolved $^{65}$Cu concentration in the range of the ambient dissolved $^{63}$Cu concentration. Only the Cu dissolved isotopic ratio data overshoot the predicted equilibrium ratio in this study. This result combined with the observation that > 99% of the Cu in South Bay has been found to be organically chelated in recent years (Beck et. al., 2002), suggests that the $^{65}$Cu spike may have overwhelmed the small excess of naturally occurring Cu-binding organic ligands present in the samples. If this was the case, then the modeled kinetic rate constants generated by the initial curve-fit solutions (solid curves) presented in Fig. 6 a-b for Cu may be skewed towards faster sorption rates by the first time series data points.

Based on this interpretation of the data, we also modeled the dissolved and particulate Cu data excluding the t = 20 minutes data points and beginning with the t = 8 hours concentrations (dashed curves, Fig. 6 a-b). These modeling results exhibited slower forward and backward sorption rate constants with higher $R^2$ values for both dissolved and particulate curve-fits (Table 3b). Comparison of these results for Cu with the original Ni kinetic results show more similar trends between metals, in terms of both sorption rate constant estimates and calculated characteristic sorption reaction times (Table 3b). This second set of Cu kinetic rate constants suggest that Cu sorption in South Bay should approach equilibrium on the order of three weeks. Ni still exhibits more sluggish sorption kinetics but the difference with Cu is less dramatic.
If the sorption process is truly first or pseudo-first order, than the reaction should follow the same kinetics during all time segments as it approaches equilibrium. To test this assumption, results were also generated for Ni and Zn where kinetic rate constant estimates were made excluding the first $t = 20$ minutes data. The results for Ni excluding the first time series data matched the original Ni rate constant estimates almost exactly. (Compare $k_f' = 0.038 \, \text{d}^{-1}$ and $k_b = 0.125 \, \text{d}^{-1}$ for dissolved Ni starting at 8 hours with $k_f' = 0.038 \, \text{d}^{-1}$ and $k_b = 0.128 \, \text{d}^{-1}$ for dissolved Ni using all of the time series data, Fig. 4a). While recent studies have found much of the dissolved Ni in South Bay to be complexed with Ethylenediaminetetraacetate (EDTA) coming from sewage treatment plants (Sedlack et al., 1997; Bedsworth and Sedlack, 1999), we do not believe that the Ni-binding organic ligands in our samples were titrated by the $^{61}$Ni addition. This is based on the observation that both the dissolved and exchangeable particulate Ni isotopic ratio data converge on the predicted equilibrium ratio as expected, and that there is no difference in the kinetic rate constant estimates found whether we include the first time series data or not.

In contrast, these results for Zn were more similar to Cu, showing higher $R^2$ values and slower sorption kinetics than originally estimated using all of the Zn time series data (dashed curves, Fig. 8). These results suggest that for Cu and Zn but not for Ni, more than one process may be controlling the dissolved and particulate concentration data in the bottle experiments. For Cu we have considered that the small excess Cu-binding organic ligand may have been titrated by the relatively large $^{65}$Cu addition, leaving some of the added Cu to adsorb as Cu$'$. Such dissolved speciation data does not exist for Zn in South Bay. Studies in Narragansett Bay, RI, have found dissolved Zn species to range from 51 to 97% organically chelated, with less organic complexation occurring in parts of the Bay where total dissolved Zn exceeded the concentration of Zn-binding organic ligands (Kozelka and Bruland, 1998). It is likely that the
case for Zn in South Bay is similar. However, the different behavior seen in the Cu and Zn isotopic ratio data relative to their predicted equilibrium ratios does not suggest that the ambient Zn-binding organic ligands were titrated in excess by the 12 nM $^{68}$Zn addition made here (compare Figs. 5c-d with 7c-d). The Zn dissolved isotopic ratio data does proceed as expected to the predicted equilibrium value (Fig. 7c). It also shows a sharp break in slope at 8 hours resulting in the large difference in the modeled rate constants for Zn excluding the $t = 20$ minutes data (Table 3).

The break in slope in the dissolved Zn isotopic ratio data and the change in estimated sorption rate constants when the first time series data are excluded could suggest that Zn sorption may possibly be more of a second order process compared to Ni (Fig. 7c and Table 3). A number of processes could be invoked to explain this pattern. Sorption and coagulation studies investigating the role of colloids on sorption kinetics have found rapid initial sorption followed by a slower reaction in the transfer of metals from dissolved to particulate pools (Honeyman and Santschi, 1989; Stordal et al., 1996; and Wen et al., 1997). In San Francisco Bay, however, colloidal (10 kDa-0.2 µm) concentrations of the metals considered here have not been found to be significant in high salinity regions such as the South Bay (<10 % for Cu, <3% for Zn and undetectable for Ni, Sanudo-Wilhelmy et al., 1996). These results do not suggest that colloids are influencing the kinetic data presented here for these metals in South Bay. More experiment replication is required to address this issue conclusively, including the use of pre-equilibrated spike additions, more time series measurements made in the first 24 hours of the experiment and measurement of the colloidal metal fraction. Regardless of these considerations, the data find Zn to have the most rapid kinetics with respect to sorption of the three metals considered, even when the initial rapid sorption portion of the time series data is excluded (Table 3).
5.3 Kinetic Results and System Response Considerations.

The kinetic results show Ni to have nearly two times slower sorption kinetics than Zn (excluding the t = 20 minutes data), with the Cu results being intermediary (Table 3b). These slower kinetics translate into different equilibration times in the South Bay, taking roughly a month to approach equilibrium for Ni, about three weeks for Cu and two weeks for Zn (estimates based on $4\tau$, Table 3b). These results suggest that dissolved and particulate Ni concentrations could show continued fluctuations for as long as a month following inputs of dissolved or particulate Ni to the Bay. In addition, if these perturbations occur in frequencies of less than a month, dissolved and particulate Ni concentrations may continue to change, never reaching equilibrium values. In contrast, given the kinetic rate constants estimated for Zn, changing fractionations of this metal should come to a new equilibrium within about half the time, following system perturbations (Table 3b).

The conceptual diagram presented in the background section graphically illustrates this point (Fig. 2). Only at times greater than $4[k'_f + k_b]^{-1}$ following a system perturbation should dissolved and particulate concentrations as well as $K_D$ values become constant. This means that sampling events following a system perturbation (at times less than $4\tau$) may detect dissolved and particulate concentrations that are quite different than equilibrium concentrations and that are likely to change if sampled again at a later time. In addition, if sampling happens to occur immediately following a system perturbation, metal fractionation results may be reversed from what the dominant system tendency may be for that metal. Depending on the magnitude and type of disturbance to the system, kinetic controls on sorption reactions may be critically relevant to interpretations of “snap-shot” samples monitoring dissolved metal concentrations and $K_D$ values made by environmental scientists.
While there are differences between metals in the time predicted to reach sorption equilibrium, there is a smaller range of values in the backward kinetic rate constant estimates than in the forward rate constant estimates (Table 3b). A similar trend is seen in the data set of Nyffeler et al., (1984). The forward kinetic rate constants for the twelve elements investigated there ranged over five orders of magnitude while the backward rate constants ranged over only one. Of the three metals studied here in South Bay, Nyffeler et al. determined kinetic rate constants for Zn only. Using radioactive $^{65}$Zn and sediments from Narragansett Bay, they found a backward rate constant of 0.32 d$^{-1}$, of the same magnitude as our 0.15 d$^{-1}$ using stable $^{68}$Zn and suspended sediments from South Bay. To compare forward rate constants we multiplied their reported $^{65}$Zn forward rate constant by their reported particle concentration giving a $k'_f$ of 0.039 d$^{-1}$ for Narragansett Bay. This is an order of magnitude smaller than the $k'_f$ of 0.12 d$^{-1}$ reported here for Zn in South Bay. This result is surprising since the particle concentration reported in Nyffeler et al., (1984) was an order of magnitude higher than that measured here and there is evidence that increasing the particle concentration can cause an increase in metal sorption forward rate constants and partition coefficients (Honeyman and Santschi, 1988).

Metal adsorption and desorption exchange rate estimates in South Bay can be calculated from the product of these kinetic constants and ambient dissolved and particulate metal concentrations (Table 3c). For the sampling event of this study, the estimated adsorption rates for both Ni and Cu are nearly 2 times larger than the estimated desorption rates. For Zn, the estimated desorption rate is larger. These exchange rate estimates, calculated on a 1-L, daily basis, illustrate that the internal cycling of metals between dissolved and particulate forms in South Bay is dynamic and can result in significant concentration fluctuations on daily time scales. This appears to be most significant for exchangeable particulate Zn, as the estimated...
daily desorption rate is roughly a fifth of the ambient exchangeable particulate concentration measured in South Bay (Table 3b).

While this study considers samples taken from only one site at one time (under late summer conditions), we can use these results to make a crude estimate of annual metal sorption exchange rates for each metal. For these preliminary estimates, a volume of $48 \times 10^7 \text{ m}^3$ water for shallow areas in South San Francisco Bay (depth of 0 – 4 m) was selected, (taken from surface area estimates by Fuller, 1982; cited in Rivera-Duarte and Flegal, 1997). Suspended particulate matter (SPM) concentrations in these shallow areas can be high due to wind induced resuspension. However, SPM concentrations similar to those measured in this study are also seen in the channels of South Bay (Schoellhamer, 1993; 1996; and Schoellhamer, USGS Water Resources of CA Web Site on Suspended-Solids Concentrations in San Francisco Bay, CA). This volume estimate, with the modeled kinetic rate constants and ambient metal concentrations (Table 3b) can be used to estimate preliminary metal adsorption and desorption exchange rates.

Order of magnitude sorption exchange rate estimates have been summarized and compared to internal and external metal fluxes reported for South Bay (Table 4). These comparisons are made to illustrate that particulate metal in the water column of South Bay is by no means inert with respect to sorption processes. The adsorption and desorption exchange rate estimates in Table 4 estimate the magnitude of each metal exchanging back and forth between dissolved and particulate forms. Ideally we would like to know the net exchange flux between dissolved and particulate metal pools by directly measuring both adsorption and desorption rates, rather than modeling the latter from adsorption data. To calculate net sorption fluxes one would also need more spatial and temporal partitioning and kinetic data obtained over a range of particle concentrations. Without such measurements, we are cautious not to calculate a net...
sorption exchange flux here. Comparisons of measured sorption exchange estimates with the internal and external metal fluxes considered in Table 4 should also be made on time scales relevant to sediment resuspension events. However, addressing these intentions requires more extensive field and laboratory investigations on benthic fluxes and sorption phenomena, numerical models incorporating sorption kinetic parameters, and measurement of external sources on short time scales throughout different seasons, the data of which does not currently exist for South Bay. Given this, it is still valuable to compare the exchange estimates made here to reported fluxes in the South Bay on an order of magnitude basis.

Table 4 indicates that the sorption exchange estimates given at the bottom of the table are of the same order of magnitude or larger than both external and internal fluxes reported in the literature for these metals in South Bay. While the combined point source loads for all three metals are the most significant external inputs to South Bay, they are of the same magnitude as our internal sorption exchange estimates. For Ni and Cu, our sorption exchange estimates are at least one order of magnitude larger than measured diffusive fluxes reported for South Bay (Kuwabara et al., 1996, and Rivera-Duarte and Flegal, 1997). For Zn the diffusive flux is of the same magnitude as the estimated Zn sorption exchange estimates. These preliminary calculations clearly indicate that dynamic internal cycling is occurring between dissolved and particulate forms on scales comparable to the loading of these metals from external and internal fluxes to South Bay.

Keen interest exists in the predictive capacity of mixing models to address metal fate and transport in contaminated estuarine systems such as the San Francisco Bay. However, the usefulness of numerical models in addressing metal partitioning in natural systems is often more limited by the availability of field data such as sorption rate constants, rather than by an ability to
develop models that reflect the complexity of estuarine environments. Wood and Babtista, (1993) and Wood et al., (1995) have developed a model of trace metal partitioning specifically for the physico-chemical environment of South San Francisco Bay. The model is diagnostic in nature with the capacity to assess kinetic controls on partition coefficients as a function of proximity to system equilibrium. The authors conclude that sorption kinetics can be responsible for variability in metal partitioning at the basin-scale in South Bay. However, they express concern that the kinetic parameters used in their model may not be representative of South Bay and emphasize the critical importance of experimentally determined site-specific rate constants to future modeling efforts and to increase the understanding of metal cycling in South Bay.

5.4 Considerations for Future Studies.

While these observations are important, especially given the paucity of kinetic data available in the oceanographic literature on metal sorption exchange in natural aquatic systems, it is also critical to keep in mind the model and geochemical assumptions used to generate these results. The experimentally derived data were modeled using equations that assume pseudo-first order kinetics for adsorption, and first order kinetics for desorption. The irreversibility and hysteresis of metal sorption was not investigated as the desorption parameters were simply modeled and not directly measured. Studies that have measured desorption rates have observed sorption irreversibility for some metals, including Zn (Duursma and Bosch, 1970; and Li et al., 1984). As this experiment was conducted under a constant particle concentration, we cannot address particle concentration effects on sorption, an important variable shown to effect sorption kinetics in laboratory experiments (Li et al., 1984; Honeyman and Santschi, 1988 and 1989).

In addition, the method used here is based on an underlying assumption that particle mass (kg) is the important particle parameter controlling metal adsorption. Especially for simple ion
exchange processes, it is likely that a metal’s partition coefficient $K_D$ will vary more as a function of the total particle surface area, rather than with the weight of particles per L water. As sorption to suspended matter can be more than simple ion exchange, concentrations of binding sites on particle surfaces is another important parameter to investigate with respect to metal partitioning. Particle organic carbon content is also likely to play a significant role in controlling $K_D$ values in addition to particle surface area (Santschi et al., 1997). Future investigations of sorption kinetics in South Bay need to include such particle characterization studies on both South Bay suspended sediments and standard reference material sediments for comparison.

To address metal sorption kinetics using a surface complexation approach, one ideally needs to quantify the sum of all available exchangeable surface sites available to bind metal in a sample of water, defined as $S'_i$ (with units of moles available sites per L water). This could be accomplished by performing a rigorous set of metal titrations using natural particles as binding ligands. $S'_i$ can be summed with the sites already occupied by adsorbed metal to estimate $S_T$, the sum total of surface sites per L water. Due to the heterogeneous nature of natural particles, $S'_i$ represents the sum of all available sites, whether on surface Fe and Mn oxide particle coatings, organic surface ligands or cation exchange sites on mineral particle surfaces. While these analyses were not included in this study, the results presented here are an important first step in establishing an overall characterization of the time scales and dynamics of metal exchange with heterogeneous suspended particles, reflective of what is happening in South Bay. To our knowledge, the kinetic rate constants reported here are currently the only ones available in the literature for South Bay, and are also the only ones available for Ni with natural particles from any bay.
6. CONCLUSIONS

A first important outcome of this study is that the Ni data set illustrates the successful application of low abundance stable isotopes and HR-ICPMS to be used as a powerful tracer technique to address complicated environmental chemistry questions. Secondly, using this application, preliminary overall, site-specific sorption kinetic rate constants have been estimated for Ni, Cu and Zn in South San Francisco Bay. A second set of sorption kinetic rate constants have been provided for Cu and Zn, based on consideration and interpretation of the Cu and Zn concentration and isotope ratio time series data. Together these results find Ni to have the most sluggish sorption kinetics, with predicted times to system equilibration with respect to sorption on the order of a month. Predicted system equilibration times are on the order of three weeks for Cu and on the order of two weeks for Zn.

Estimates of exchange rates between dissolved and particulate forms calculated using these rate constants indicate that sorption processes can cause dynamic internal cycling of these metals in South Bay, resulting in concentration fluctuations that can be significant, even on daily time scales. Preliminary estimates of the dynamic exchange of metal between dissolved and particulate forms are found to be of the same order of magnitude or larger than reported benthic fluxes and external sources of these metals to South Bay. While future modeling efforts are required to address net sorption fluxes of metals on different time scales of significance in the Bay, these conclusions are a significant first step in providing the site-specific sorption kinetic rate constant estimates essential for such models. In addition, up until now, the role of sorption exchange in the internal cycling of metals in the water column of South San Francisco Bay has remained largely unaddressed, despite its crucial importance, due to the challenges associated with quantifying sorption processes on natural, heterogeneous particles.
Acknowledgements—We wish to thank R. Franks of the UCSC Marine Analytical Laboratory for assistance with ICPMS analyses and G. Smith of the UCSC Institute of Marine Sciences for support with wet chemistry procedures. Our sincere thanks go to A. R. Flegal and I. Rivera-Duarte of the UCSC Environmental Toxicology Department for sampling support in South Bay. We thank R. S. Anderson of the UCSC Earth Sciences Department for his assistance with the data modeling procedure. We are grateful to the Harbor Processes Program of the Office of Naval Research Grant #N00014-99-1-0035 for funding this research. Finally we would sincerely like to thank two anonymous reviewers of the originally submitted manuscript for their detailed and thoughtful comments.
7. REFERENCES


Table 1. Comparison of Certified Concentrations and Organic Extraction Results.

<table>
<thead>
<tr>
<th>CASS-3 Certified Concentrations (nM)</th>
<th>Organic Extraction Results (nM)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mn</td>
<td>45.7 ± 6.6</td>
</tr>
<tr>
<td>Fe</td>
<td>22.6 ± 3.0</td>
</tr>
<tr>
<td>Co</td>
<td>0.70 ± 0.15</td>
</tr>
<tr>
<td>Ni</td>
<td>6.58 ± 1.1</td>
</tr>
<tr>
<td>Cu</td>
<td>8.14 ± 1.0</td>
</tr>
<tr>
<td>Zn</td>
<td>19.0 ± 3.8</td>
</tr>
</tbody>
</table>

(n = 3)  
± 95% confidence limits  ± 1 standard deviation
Table 2. Time Series Results of Two Week Sorption Experiment: Distribution Coefficients and Metal Fractionations.

<table>
<thead>
<tr>
<th></th>
<th>Nickel</th>
<th>Copper</th>
<th>Zinc</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Ambient) (20 minutes) (14 days)</td>
<td>(Ambient) (20 minutes) (14 days)</td>
<td>(Ambient) (20 minutes) (10 days)</td>
<td></td>
</tr>
<tr>
<td>$K_D = 10^{3.65} \text{ L kg}^{-1}$</td>
<td>$K_D = 10^{3.49} \text{ L kg}^{-1}$</td>
<td>$K_D = 10^{4.52} \text{ L kg}^{-1}$</td>
<td></td>
</tr>
<tr>
<td>86.6% Dissolved</td>
<td>90.3% Dissolved</td>
<td>59.2% Dissolved</td>
<td></td>
</tr>
<tr>
<td>$K_D = 10^{3.49} \text{ L kg}^{-1}$</td>
<td>$K_D = 10^{3.85} \text{ L kg}^{-1}$</td>
<td>$K_D = 10^{4.30} \text{ L kg}^{-1}$</td>
<td></td>
</tr>
<tr>
<td>80.4% Dissolved</td>
<td>80.4% Dissolved</td>
<td>44.9% Dissolved</td>
<td></td>
</tr>
<tr>
<td>$K_D = 10^{4.21} \text{ L kg}^{-1}$</td>
<td>$K_D = 10^{4.35} \text{ L kg}^{-1}$</td>
<td>$K_D = 10^{4.55} \text{ L kg}^{-1}$</td>
<td></td>
</tr>
<tr>
<td>79.2% Dissolved</td>
<td>82.4% Dissolved</td>
<td>46.7% Dissolved</td>
<td></td>
</tr>
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</table>
Table 3. Sorption Reaction Time Scale and Exchange Rate Estimates for South San Francisco Bay (per L per day).

<table>
<thead>
<tr>
<th></th>
<th>Modeled Forward Rate Constant</th>
<th>Modeled Backward Rate Constant</th>
<th>Characteristic Reaction Time</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$k'_f$</td>
<td>$k_b$</td>
<td>$\tau = [k'_f + k_b]^{-1}$</td>
</tr>
<tr>
<td>Ni</td>
<td>0.032 d$^{-1}$</td>
<td>0.13 d$^{-1}$</td>
<td>R$^2$=0.96 6.3 d</td>
</tr>
<tr>
<td>Cu$^a$</td>
<td>0.20 d$^{-1}$</td>
<td>0.43 d$^{-1}$</td>
<td>R$^2$=0.90 1.6 d</td>
</tr>
<tr>
<td>Zn$^a$</td>
<td>0.30 d$^{-1}$</td>
<td>0.39 d$^{-1}$</td>
<td>R$^2$=0.90 1.5 d</td>
</tr>
<tr>
<td>Ni</td>
<td>0.032 d$^{-1}$</td>
<td>0.13 d$^{-1}$</td>
<td>R$^2$=0.96 6.3 d</td>
</tr>
<tr>
<td>Cu$^b$</td>
<td>0.068 d$^{-1}$</td>
<td>0.12 d$^{-1}$</td>
<td>R$^2$=0.96 5.3 d</td>
</tr>
<tr>
<td>Zn$^b$</td>
<td>0.121 d$^{-1}$</td>
<td>0.15 d$^{-1}$</td>
<td>R$^2$=0.96 3.7 d</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>Ambient Concentrations</th>
<th>Adsorption Rate Estimate</th>
<th>Modeled Desorption Rate Estimate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni</td>
<td>[M$_d$] 56 nM [M$_p$] 8 nM</td>
<td>$k'_f$ • [M$_d$] = 1.8 nM d$^{-1}$</td>
<td>$k_b$ • [M$_p$] = 1.0 nM d$^{-1}$</td>
</tr>
<tr>
<td>Cu$^b$</td>
<td>58 nM 15 nM</td>
<td>3.9 nM d$^{-1}$</td>
<td>1.8 nM d$^{-1}$</td>
</tr>
<tr>
<td>Zn$^b$</td>
<td>14 nM 16 nM</td>
<td>1.7 nM d$^{-1}$</td>
<td>2.4 nM d$^{-1}$</td>
</tr>
</tbody>
</table>

(a) Kinetic rate constants from initial Cu and Zn data models (Figs. 6 and 8, solid curves).
(b) Kinetic rate constants from modeling of dissolved and particulate Cu and Zn data, excluding the t = 20 minutes data points and beginning with t = 8 hours (Figs. 6 and 8, dashed curves).
Table 4. Comparisons of Metal Cycling Processes in South San Francisco Bay

<table>
<thead>
<tr>
<th></th>
<th>Nickel</th>
<th>Copper</th>
<th>Zinc</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>External Fluxes (Inputs) from</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Atmosphere</td>
<td>700 kg/y</td>
<td>3,700 kg/y</td>
<td>19,000 kg/y&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
<tr>
<td>Tributaries</td>
<td>5,000 kg/y</td>
<td>5,000 kg/y</td>
<td>7,200 kg/y&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
<tr>
<td>Combined Point Sources</td>
<td>15,000 kg/y</td>
<td>16,800 kg/y</td>
<td>36,000 kg/y&lt;sup&gt;c&lt;/sup&gt;</td>
</tr>
<tr>
<td><strong>Internal Fluxes to the Water Column</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Diffusive Benthic Flux</td>
<td>5,000 kg/y</td>
<td>860 kg/y</td>
<td>27,000 kg/y&lt;sup&gt;d&lt;/sup&gt;</td>
</tr>
<tr>
<td><strong>Sorption Exchange Rates in the Water Column</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Adsorption Exchange Rate Estimate</td>
<td>18,000 kg/y</td>
<td>44,000 kg/y</td>
<td>19,000 kg/y&lt;sup&gt;e&lt;/sup&gt;</td>
</tr>
<tr>
<td>Desorption Exchange Rate Estimate</td>
<td>12,000 kg/y</td>
<td>20,000 kg/y</td>
<td>27,000 kg/y&lt;sup&gt;e&lt;/sup&gt;</td>
</tr>
</tbody>
</table>

References refer to all data reported in individual rows of the table.

<sup>a</sup> Estimated atmospheric inputs based on deposition rates measured in other parts of the US (Gunther et al., 1987; cited in Rivera-Duarte and Flegal, 1997).

<sup>b</sup> Average river concentration times average river discharge (Rivera-Duarte and Flegal, 1997).

<sup>c</sup> Estimated loads entering South Bay from point sources (Davis J. A. et al., 1991; cited in Rivera-Duarte and Flegal, 1997).

<sup>d</sup> Average diffusive benthic flux calculated using data from two contaminated sample locations in South Bay (Rivera-Duarte and Flegal, 1997) and the volume of water in South Bay “shallows” (0 – 4 m depth).

<sup>e</sup> This study, calculated using the volume of water in South Bay “shallows” (0 – 4 m depth), roughly an eighth of the total volume in South Bay. Cu and Zn sorption flux estimates were calculated using kinetic rate constants from modeling of dissolved and particulate data excluding t=20 minutes data points and beginning with t=8 hours data (Table 3b).
FIGURE LEGENDS

Fig. 1. Study location map of the San Francisco Bay Estuary. The water collection location is indicated by the solid circle, located near the Dumbarton Bridge in the South Bay.

Fig. 2. (a) The dissolved metal concentration \([M_d]\), the exchangeable particulate metal concentration \([M_p]\) and (b) the distribution ratio \(K_D\) as a function of time with the particle concentration held constant. At \(t = 0\) an addition of dissolved metal is made. The system reaches equilibrium at approximately \(4(k'_f + k_b)^{-1}\).

Fig. 3. Nickel isotope data as a function of time. (a) Dissolved and (b-c) particulate isotope concentration data of Ni\(^{61}\) (closed triangles), Ni\(^{58}\) (open circles), Ni\(^{60}\) (open diamonds) and Ni\(^{62}\) (open squares). The arrow in 3a symbolizes the magnitude of the Ni\(^{61}\) spike addition made up from initial ambient concentrations. (d) Dissolved and (e) particulate isotope concentration ratio data of Ni\(^{61}/Ni^{60}\) (closed triangles) and Ni\(^{62}/Ni^{60}\) (open squares). The * below the abscissa indicates the initial ambient isotope concentrations and ratios while the + indicates the natural abundance isotope concentration ratios. The dashed horizontal lines in 3d-e indicate the predicted equilibrium ratio.

Fig. 4. Best curve-fit models of (a) dissolved and (b) exchangeable particulate Ni\(^{61}\) concentration data. The results of the independent model solutions are presented in the embedded tables. Equations 10 and 12 were used to model the data as presented in section 2.

Fig. 5. Copper isotope data as a function of time. (a) Dissolved and (b) particulate isotope concentration data of Cu\(^{65}\) (closed triangles) and Cu\(^{63}\) (open diamonds). The arrow in 5a symbolizes the magnitude of the Cu\(^{65}\) spike addition made up from initial ambient concentrations. (c) Dissolved and (d-e) particulate isotope concentration ratio data of Cu\(^{65}/Cu^{63}\) (closed triangles). (The *, + and dashed horizontal lines are as in Fig. 3).

Fig. 6. Best curve-fit models of (a) dissolved and (b) exchangeable particulate Cu\(^{65}\) concentration data. The solid curves are the best fits found using all of the time series data. The dashed curves are the best fits found, excluding the t=20 minutes data and beginning with the t=8 hours data. The results of the independent model solutions are presented in the embedded tables.

Fig. 7. Zinc isotope data as a function of time. (a) Dissolved and (b) particulate isotope concentration data of Zn\(^{68}\) (closed triangles), Zn\(^{67}\) (open circles), Zn\(^{66}\) (open diamonds), and Zn\(^{64}\) (open squares). The arrow in 7a symbolizes the magnitude of the Zn\(^{68}\) spike addition made up from initial ambient concentrations. (c) Dissolved and (d-e) particulate isotope concentration ratio data of Zn\(^{68}/Zn^{64}\) (closed triangles), Zn\(^{67}/Zn^{64}\) (open circles) and Zn\(^{66}/Zn^{64}\) (open diamonds). (The *, + and dashed horizontal lines are as in Fig. 3).

Fig. 8. Best curve-fit models of (a) dissolved and (b) exchangeable particulate Zn\(^{68}\) concentration data. The solid curves are the best fits found using all of the time series data. The dashed curves are the best fits found, excluding the t=20 minutes data and beginning with the t=8 hours data. The results of the independent model solutions are presented in the embedded tables.
\[ \frac{\sim 4}{k_f + k_b} \]

\[ t = 0 \]

\[ K_D(t = 0) \]

\[ K_D(t \to \infty) \]

\[ [M_p]_i \]

\[ [M_d]_i \]

\[ [M_p]_{eq} \]

\[ [M_d]_{eq} \]
**Dissolved $^{61}$Ni**

![Graph showing the decrease in dissolved $^{61}$Ni with time.](image)

<table>
<thead>
<tr>
<th>Value</th>
<th>Error</th>
</tr>
</thead>
<tbody>
<tr>
<td>$k_f$</td>
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<tr>
<td>$k_b$</td>
<td>0.128</td>
</tr>
<tr>
<td>$R^2$</td>
<td>0.959</td>
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</table>

**Particulate $^{61}$Ni**

![Graph showing the increase in particulate $^{61}$Ni with time.](image)

<table>
<thead>
<tr>
<th>Value</th>
<th>Error</th>
</tr>
</thead>
<tbody>
<tr>
<td>$k_f$</td>
<td>0.026</td>
</tr>
<tr>
<td>$k_b$</td>
<td>0.131</td>
</tr>
<tr>
<td>$R^2$</td>
<td>0.969</td>
</tr>
</tbody>
</table>

Figure 4 a-b

Gee and Bruland

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Figure 5 a-e  

Gee and Bruland
Figure 6 a-b

Gee and Bruland

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Figure 8 a-b  
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