Sources and Environmental Fate of Strongly Complexed Nickel in Estuarine Waters: The Role of Ethylenediaminetetraacetate

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D A V I D   L.   S E D L A K *

*Department of Civil and Environmental Engineering,
University of California, Berkeley,
Berkeley, California 94720-1710*

Measurements of Ni speciation made by competitive ligand exchange techniques indicate that a significant portion of the dissolved Ni in surface waters, wastewater effluents, and surface runoff is complexed by an extremely strong ligand. To identify this ligand, its sources, and environmental fate, simultaneous measurements of nickel ethylenediaminetetraacetate ($NiEDTA^{2-}$) by HPLC and Ni speciation by cathodic stripping voltammetry and chelating resin column partitioning are compared. Analysis of municipal wastewater effluents indicate that $NiEDTA^{2-}$ accounts for the strongly complexed Ni in wastewater effluent, even when there are few industrial sources of EDTA. Experiments conducted in natural water samples indicate that exchange kinetics have a profound impact on the results of cathodic stripping voltammetry speciation measurements, causing $NiEDTA^{2-}$ complexes to appear stronger than would be predicted by equilibrium calculations. Measurements of Ni speciation in San Francisco Bay indicate a seasonal variation consistent with the discharge of stable $NiEDTA^{2-}$ from wastewater effluents and weaker Ni complexes from surface runoff. The presence of nonreactive, nonbioavailable $NiEDTA^{2-}$ complexes should be considered in geochemical models and in the development of site-specific water quality objectives.

Introduction

The environmental fate and effects of pollutant metals depend on speciation. In the case of metal cations, complexation by organic ligands generally lowers their affinity for surfaces, leading to their passage through wastewater treatment systems and an enhancement of their mobility in aquatic systems (*1–4*). Complexation also reduces the toxicity of many pollutant metals to aquatic organisms (*5–8*). Because complexation plays such an important role in the behavior of pollutant metals, considerable effort has been directed toward the measurement of metal speciation.

Most analytical techniques for determining metal speciation yield operationally defined measurements of various classes of metal species. Electrochemical and competitive ligand exchange techniques (*9–13*) distinguish between labile metal species (i.e., metal cations, inorganic complexes, and weak metal–organo complexes; $K^{cond} < 10^5$), moderately strong complexes (e.g., metal complexes with humic sub-

stances; $K^{cond} \approx 10^5-10^{12}$), and strongly complexed metal species (e.g., metals complexed by polydentate ligands; $K^{cond} > 10^{12}$). Ultrafiltration distinguishes between metal species of different sizes (*14, 15*). Unfortunately, the limitations of these operational definitions restrict our ability to prevent the discharge of metals, to predict their fate, and to develop speciation-based water quality criteria.

In our previous work (*16*), we established that most of the dissolved Ni in the effluent of municipal wastewater treatment plants is discharged in the form of a strong complex, whereas most of the dissolved Ni in surface runoff consists of moderately strong complexes. Analysis of competitive ligand exchange–cathodic stripping voltammetry (CLE-CSV) data indicated that the Ni complex detected in wastewater effluent was extremely strong (i.e., $K^{cond} > 4.0 \times 10^{12} \, M^{-1}$) and did not dissociate when mixed with seawater. However, changes in Ni speciation observed when samples were driven to equilibrium by heating to 90 °C prior to analysis suggested that the system was not at equilibrium. The differences in dissolved Ni speciation between the two sources led us to hypothesize that seasonal variations should be evident in Ni speciation in San Francisco Bay, with relative concentrations of strongly complexed Ni increasing in summer, when surface runoff discharges decrease.

A review of data on chemical use patterns and the chemical properties of synthetic chelating agents indicates that ethylenediaminetetraacetate (EDTA) is the compound most likely responsible for complexation of Ni in wastewater effluent. EDTA has been detected in wastewater effluents at concentrations as high as 19 μM (*17–19*), whereas concentrations of other chelating agents are typically at least an order of magnitude lower (*17, 20*) because they are used in smaller quantities (*21*) and are partially or completely removed during wastewater treatment (*17, 20, 22, 23*).

If the strongly complexed Ni in wastewater effluent is $NiEDTA^{2-}$, some assumptions about the biogeochemistry of Ni in San Francisco Bay and other surface waters must be reexamined. For example, it is generally assumed that the strongly complexed Ni in polluted waters could not be $NiEDTA^{2-}$ because the competitive ligand used in the CLE-CSV analysis (i.e., dimethylglyoxime) should outcompete EDTA in seawater (*24*). However, if the Ni complex is $NiEDTA^{2-}$, equilibrium analyses of CLE-CSV data could be incorrect because Ni–ligand exchange reactions are extremely slow (*25, 26*). Thus, $NiEDTA^{2-}$ complexes could appear to be stronger than predicted by equilibrium considerations.

To test the hypothesis that the strongly complexed Ni in wastewater effluent is $NiEDTA^{2-}$, a highly sensitive HPLC method was used to measure $NiEDTA^{2-}$. Analyses of Ni speciation by competitive ligand exchange were compared with HPLC analyses in an attempt to account for all of the strong Ni complexes. Experiments were also performed to assess the role of kinetics in Ni speciation measurements. After confirming that $NiEDTA^{2-}$ is the strongly complexed Ni species in wastewater effluent, the speciation of Ni in San Francisco Bay was measured during three seasons to test the hypothesis that Ni speciation in San Francisco Bay is affected by the relative contributions of wastewater effluent and surface runoff.

Materials and Methods

Chemicals. Unless otherwise specified, all chemicals were purchased from Fisher Scientific. Most solutions were prepared by dissolving chemicals of the highest available purity in Milli-Q water. Stock solutions of 0.1 M dimeth-

* Corresponding author e-mail: sedlak@ce.berkeley.edu; telephone: (510) 643-0256; fax: (510) 642-7483.

| name (location)	design flow (m³/s) ([MGD])	industrial contribution (% of flow)	biological treatment	advanced biological treatment	advanced physical treatment
SJSC (San Jose)	7.3 [167]	11	air-activated sludge	nitrification with some denitrification and phosphorus removal	effluent filtration
EBMUD (Oakland)	5.3 [120]	10.5	oxygen-activated sludge		
MVSD (Martinez)	0.07 [1.5]	<1	trickling filter		
DSR (Dublin)	0.5 [11.5]	<5	air-activated sludge		
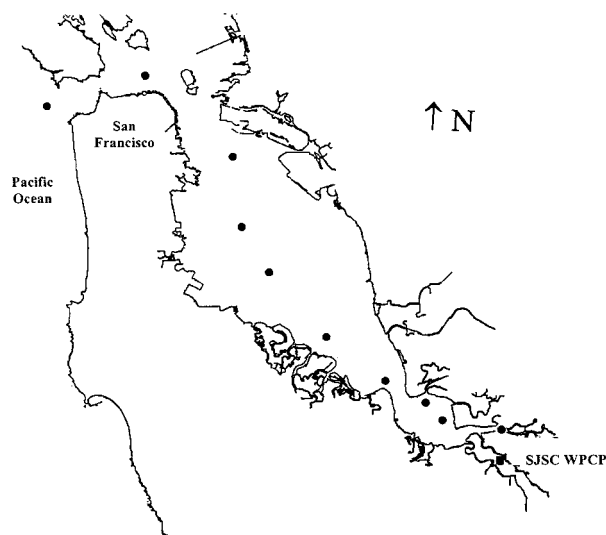
FIGURE 1. Location of surface water sampling sites in San Francisco Bay and of the San Jose/Santa Clara Water Pollution Control Plant (SJSC WPCP).

ylglyoxime (DMG) were prepared in methanol (HPLC grade). In several cases, microbial growth was evident after equilibration of samples with DMG in methanol. In these samples, microbial growth was prevented by dissolving DMG in methyl *tert*-butyl ether (Aldrich Chemical Co.).

All bottles, filters, and tubing used for sample collection or storage were made of Teflon, polypropylene, or polyethylene. Prior to use, all equipment that came into contact with the samples was cleaned in Micro Detergent (Baxter Scientific), rinsed in methanol (HPLC grade), and soaked in 2 N HCl (reagent grade) for 1 week.

Study Site and Sample Collection. Wastewater effluent samples were collected between December 1996 and September 1997 from four water pollution control plants (WPCPs) in the San Francisco Bay area (Table 1). Two of these facilities [i.e., San Jose/Santa Clara (SJSC) and East Bay Municipal Utilities District (EBMUD)] receive significant discharges from industries that use metals and chelating agents (e.g., metal plating and computer disk manufacturing). The other two facilities [i.e., Dublin/San Ramon (DSR) and Mountain View Sanitary District (MVSD)] do not receive significant amounts of industrial wastewater. Industrial wastewater 24-h composite samples also were collected (ISCO composite sampler) from seven industrial facilities discharging to the SJSC WPCP. Wastewater effluent was collected using trace metal clean procedures (27). Samples were collected in acid-cleaned double-bagged bottles and stored at 4 °C until analysis.

Surface water samples from San Francisco Bay were collected January 21–24, April 15–17, and July 28–30, 1997, as part of the Regional Monitoring Program for Trace Substances (28) (Figure 1). Samples were stored in acid-cleaned double-bagged bottles at −5 °C until analysis.

Total Dissolved Ni. In most samples, [Ni_{diss}] was determined in 0.45-μm-filtered samples by graphite furnace atomic absorption spectroscopy (GFAAS) using standard conditions (29). Previous results using dialysis membranes (16) indicate that the concentration of colloidal Ni in effluent from these treatment plants is negligible. Samples were analyzed in duplicate by standard additions. Quality assurance samples (NIST SRM 1643d, trace elements in water) and method blanks also were analyzed.

[Ni_{diss}] in samples from San Francisco Bay and two of the treatment plants could not be determined with sufficient precision by GFAAS because concentrations were near or below the limit of quantification. In these samples, [Ni_{diss}] was determined using CLE-CSV after UV oxidation of the organic ligands as described previously (16).

Measurements of Ni Speciation by Competitive Ligand Exchange. The concentration of Ni that was not associated with strong ligands was determined by CLE-CSV using DMG as a competing ligand as described previously (16).

The speciation of Ni was also determined using chelating resin column partitioning−graphite furnace atomic absorption spectroscopy (CRCP-GFAAS) as described previously (16). Our previous results indicated that only uncomplexed and weakly complexed forms of Ni were retained by the resin when high flow rates were used. To differentiate between strong and moderately strong Ni complexes, the flow rate was varied from 0.8 to 27 mL min^{-1}. At the lowest flow rate, the contact time with the chelating resin was long, allowing the resin to retain all but the very strong complexes. Thus, measurement at high and low flow rates provided a means of distinguishing between weak (including uncomplexed) and moderately strong Ni complexes.

Analysis of Total EDTA, NiEDTA²⁻, and FeEDTA⁻. To quantify EDTA species, a previously published HPLC/UV technique developed for use in wastewater (19) was modified to enhance its sensitivity for NiEDTA²⁻. Although GC methods have been used to detect EDTA in wastewater (17, 18), the derivitization required prior to analysis results in dissociation of the metal−EDTA complexes. Therefore, GC methods are not suitable for determining EDTA speciation.

For total EDTA analysis, a 1-mL sample was placed in a Teflon beaker and evaporated to dryness in a vacuum oven at 60 °C. The sample was redissolved in formate buffer ([$HCOO^-$]$_{tot}$ = 20 mM) at pH 3.3. Fe(NO₃)₃ was then added to the sample (1000 mg L^{-1} reference standard, diluted to yield a final concentration of 10 μM). Previous experiments have verified that the combination of excess Fe(III) and low pH results in the conversion of all relevant MeEDTA species, except kinetically inert NiEDTA²⁻ and CrEDTA⁻, to FeEDTA⁻ (19). The FeEDTA⁻ complex was then detected after separation by reverse-phase ion-pair chromatography (Supelcosil LC-18 column; eluent, 20 mM formate buffer, 1 mM tetrabutylammonium bromide, 9% acetonitrile) with UV detection at 258 nm. A diode array detector (Gynkotek UVD 320) was used to confirm the identity of FeEDTA⁻ peaks. Because the conversion of NiEDTA²⁻ and CrEDTA⁻ to FeEDTA⁻ is slow and the compounds do not absorb light strongly at 258 nm, Ni and Cr complexes with EDTA are not detected by this method. [EDTA]$_{tot}$ (i.e., all forms of EDTA except CrEDTA⁻) was calculated by adding the concentration

measured by this technique to [NiEDTA^{2-}] measured in the manner described below.

To quantify NiEDTA^{2-}, the sample was prepared as described above. After all metal—EDTA species (excluding NiEDTA^{2-} and CrEDTA$^-$) were converted into FeEDTA$^-$, the sample was irradiated in a glass vial with a 500-W Hg lamp for 30 min. Because FeEDTA$^-$ is degraded by visible light through a ligand-to-metal-charge-transfer reaction (*30*), all of the non-Ni EDTA species were removed from the sample by irradiation. CrEDTA$^-$ is neither removed by visible light irradiation nor transformed to FeEDTA$^-$ after irradiation; thus, CrEDTA$^-$ does not interfere with the measurement of NiEDTA^{2-}. Once the other forms of EDTA were removed, NiEDTA^{2-} was converted into FeEDTA$^-$ by heating the sample in a sealed vial to 100 °C for 3.5 h. Previous experiments have verified that NiEDTA^{2-} is quantitatively converted to FeEDTA$^-$ by this process (*19*). At this point, [FeEDTA$^-$], as determined by HPLC, corresponds to [NiEDTA^{2-}] originally present in the sample.

[FeEDTA$^-$] originally present in the sample was quantified by irradiating the samples with visible light prior to addition of formate buffer and Fe(III) solution. The difference in signal between this sample and the total EDTA sample corresponds to [FeEDTA$^-$] originally present.

In all experiments, EDTA and NiEDTA^{2-} recoveries were evaluated using controls consisting of 100 nM each of FeEDTA$^-$ in Milli-Q water, NiEDTA^{2-} in Milli-Q water, and NiEDTA^{2-} added to the samples. Recovery of FeEDTA$^-$ and NiEDTA^{2-} in Milli-Q water ranged from 85 to 105%. Recoveries of NiEDTA^{2-} in the wastewater effluent samples ranged from 70 to 100%. Analysis of samples by standard additions indicated that the matrix did not affect the sensitivity of the method. The detection limit for NiEDTA^{2-} was ~20 nM in wastewater effluent (signal of the blank + 3σ), on the basis of the standard deviation of 53 injections of photolyzed wastewater. Due to interferences related to the ion-pairing agent, HPLC measurements of EDTA could not be performed in seawater.

Results

Dissolved Ni Concentration. [Ni]$_{diss}$ in the effluent from the four WPCPs exhibited distinct differences between the plants receiving industrial discharges and those receiving only domestic wastewater (Figure 2a). The industrially influenced plants (i.e., SJSC and EBMUD) had [Ni]$_{diss}$ values that were approximately twice as high as those of the other plants (mean [Ni]$_{diss}$ = 140 vs 67 nM). [Ni]$_{diss}$ in San Francisco Bay showed a general trend of decreasing concentration with increasing salinity (Figure 3). [Ni]$_{diss}$ ranged from ~160 nM in the low-salinity samples collected from South San Francisco Bay in July to 5 nM in the saline samples collected at the Golden Gate site.

Measurements of Nickel Speciation by Competitive Ligand Techniques. Data from CLE-CSV and CRCP-GFAAS were analyzed as described previously (*16*). Variations in DMG concentration from 0.1 to 1 mM and equilibration time from 12 h to 7 days had no effect on CLE-CSV results. Consistent with our previous results (*16*), strongly complexed Ni (i.e., NiL$_1$) accounted for 55–70% of the Ni$_{diss}$ discharged by the WPCPs (Figure 2a). NiL$_1$ also accounted for 53 ± 25% of Ni$_{diss}$ in the three southernmost sites in San Francisco Bay and for 0–91% of the Ni from the other sites in San Francisco Bay (Figure 3).

Titration of wastewater effluent with Ni for CRCP-GFAAS yielded different results from titrations of surface water samples. In wastewater samples, slopes of titration curves were not equal to unity until [Ni]$_{diss}$ exceeded 300–600 nM. As we determined previously (*16*), these results indicate the presence of moderately strong Ni complexing ligands with
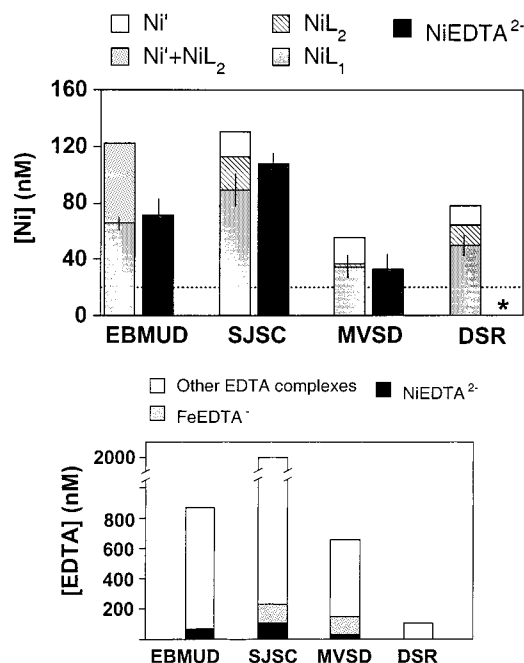
FIGURE 2. (a, top) Comparison of Ni speciation by competitive ligand techniques to NiEDTA^{2-} in four water pollution control plants. For abbreviations and description, see Table 1. Vertical lines indicate 1 standard deviation. Dashed line indicates detection limit for NiEDTA^{2-}. *, not detected. (b, bottom) Concentration of metal—EDTA complexes in wastewater effluent.
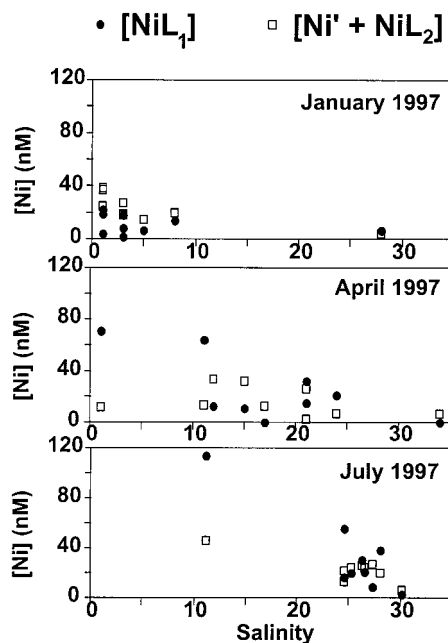

FIGURE 3. Concentration of dissolved Ni species in San Francisco Bay as a function of salinity as determined by CLE-CSV. Data were collected at a depth of 1 m on a transect running from San Jose to the Golden Gate bridge (see Figure 1).

$K_{NiL_1}^{cond} \approx 10^7$ M^{-1}. In contrast, surface water samples exhibited a linear relationship, similar to results reported by Donat et al. (*9*).

In all samples to which Ni had not been added prior to analysis, a small percentage of the Ni present in the sample was retained on the chelating resin column. When a high pumping rate was used, this value, referred to as Ni$_{CRCP}'$, represents the amount of metal present as Ni^{2+}, inorganic complexes, and weak organocomplexes that are CRCP-labile.
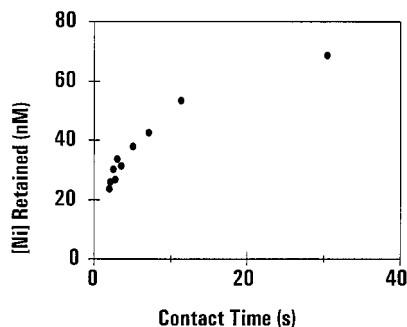
FIGURE 4. [Ni] retained on the CRCP resin as a function of sample contact time for a filtered effluent sample from the SJSC WPCP. $[Ni]_{diss} = 150$ nM.

These data can be used to estimate the concentration of moderately strong Ni complexes (i.e., NiL_2) (16). NiL_2 accounted for an average of ~14 ± 10% of the dissolved Ni present in the wastewater effluent samples (Figure 2a) but was not detected in samples from San Francisco Bay.

In wastewater effluents, as the contact time increased, more Ni was retained on the resin column (Figure 4). The maximum concentration of Ni retained by the column is comparable to the labile Ni measured by CLE-CSV (i.e., Ni^*_{CSV}) and can be used to estimate NiL_1. Estimates of NiL_1 obtained by using this method were not significantly different from estimates obtained by CLE-CSV, except for the sample from EBMUD. For this sample, CRCP-GFAAS yielded an estimate of NiL_1 of 90 nM, whereas results from CLE-CSV indicate a concentration of 65 nM. This relatively small discrepancy could be attributable to the presence of a small amount of a Ni complex that is not retained by the resin but is capable of forming complexes with DMG.

Component Addition Sequence. Due to the slow kinetics of Ni complex dissociation, the effect of component addition sequence on CLE-CSV measurements was evaluated. CLE-CSV measurements were performed by adding EDTA and DMG in a different order to samples with otherwise identical compositions. In one set of experiments, 250 μM DMG was added to 100 nM $NiEDTA^{2-}$ pre-equilibrated in UV-oxidized seawater. Under these conditions, $Ni(DMG)_2$ was not formed (i.e., no signal was measured by CLE-CSV). In another set of experiments, 100 nM EDTA was added to UV-oxidized seawater in which 100 nM Ni and 250 μM DMG had already equilibrated. In this experiment, no $NiEDTA^{2-}$ was formed [i.e., a signal corresponding to 100 nM $Ni(DMG)_2$ was detected].

EDTA Analyses. [EDTA] in effluent samples from the four WPCPs ranged from approximately 100 to 2000 nM (Figure 2b). The highest [EDTA] was consistently observed at the SJSC WPCP, which receives a substantial amount of industrial discharge from industries that use chelating agents (range for samples collected on three different dates = 1050−1925 nM). The lowest [EDTA] was consistently observed at the DSR WPCP, which serves few industries (range for samples collected on three different dates = 100−400 nM). $FeEDTA^-$ was detected only at the SJSC and MVSD WPCPs, where it accounted for 10−20% of the total EDTA in the samples. $NiEDTA^{2-}$ accounted for 5−9% of the total EDTA in the samples from all facilities except DSR, where it was not detected in any of the three samples collected from the plant.

Industrial Samples. Between 35 and 100% of the Ni discharged by industrial wastewater treatment plants was present as NiL_1 (Table 2). At the four facilities where $NiEDTA^{2-}$ also was measured, results indicate that NiL_1 is $NiEDTA^{2-}$. [EDTA] varied by the type of industry ([EDTA]$_{tot}$ = 280−>50000 nM), with the highest concentrations in effluent from printed circuit board manufacturers.

Discussion

To use information on Ni speciation to reduce the discharge of Ni, to improve geochemical models, or to develop site-specific water quality criteria, it is necessary to understand the behavior of NiL_1 complexes. Specifically, the identity of L_1 and its source must be determined and its stability and fate in the aquatic environment must be assessed. Each of these issues is discussed below.

Ligand Identity. Our data indicate that $NiEDTA^{2-}$ is the strong Ni complex discharged by three of the four WPCPs. Comparison of the two different competitive ligand exchange speciation measurements with direct measurement of $NiEDTA^{2-}$ (Figure 2a) indicates that NiL_1 is $NiEDTA^{2-}$ at the SJSC, EBMUD, and MVSD WPCPs. At the DSR WPCP, [$NiEDTA^{2-}$] was below the limit of quantification for the HPLC method in all samples. Because there is a significant amount of strongly complexed Ni at this location, it is possible that a strong ligand other than EDTA is present at ~40−60 nM. However, manufacturing data (21), previous studies of the fate of synthetic chelating agents in WPCPs (17, 20, 22, 23), and measurements of Ni speciation at the other facilities indicate that it is unlikely that other synthetic chelating agents could be present at these concentrations in wastewater effluent.

Comparison of Ni speciation in wastewater influent and effluent indicates that NiL_1 is neither formed nor removed in the treatment plants: [NiL_1], as measured by CRCP and CLE-CSV, is nearly identical in the influent and effluent of all four treatment plants (31). This suggests that Ni enters the treatment plant in a complexed form. This is consistent with previous studies (17−19, 32) that indicate that metal−EDTA complexes are neither degraded nor removed in wastewater treatment plants.

Previous studies of Ni speciation in San Francisco Bay and other estuaries also have indicated the presence of significant concentrations of strongly complexed Ni (9, 11, 24, 33−35). The conditional stability constant (K^{cond}) of the observed ligand was estimated to be $>10^{18}$ M^{-1} (24). Given this equilibrium constant, one would predict that the ligand detected in natural waters could not be EDTA (i.e., the conditional stability constant for $NiEDTA^{2-}$ in seawater is ~10^{10} M^{-1}). However, equilibrium calculations do not consider the slow kinetics of Ni−ligand complex formation and dissociation (25, 26). Estimates of K^{cond} derived from CLE-CSV measurements assume that equilibrium is reached between the competing ligand and the ligands present in the sample. Our results indicate that equilibrium is not achieved when $NiEDTA^{2-}$ is present unless the sample is heated to drive it to equilibrium. Once $NiEDTA^{2-}$ is formed, it does not dissociate during overnight equilibration at room temperature. Similar effects have been noted in the adsorption of $NiEDTA^{2-}$ complexes by iron oxides (36).

Our experiments confirm that component addition sequence affects the results of the CLE-CSV experiments. Under the conditions encountered in the CLE-CSV experiments performed in San Francisco Bay water (i.e., DMG added to a preformed $NiEDTA^{2-}$ complex), $NiEDTA^{2-}$ appeared to be stronger than predicted by equilibrium calculations due to slow exchange reactions of the $NiEDTA^{2-}$ complex. Experiments performed in which similar concentrations of DMG and EDTA were added to UV-oxidized seawater also confirm the effect of addition sequence: the first ligand added is not displaced by the second due to kinetic limitations. These experiments show that an equilibrium approach to analysis of metal speciation data is inappropriate in the case of metals such as Ni that exhibit slow exchange kinetics.

Ligand Source. Measurements of [EDTA] and [$NiEDTA^{2-}$] provide insight into the origin of strongly complexed Ni. The detection of EDTA at all of the WPCPs indicates that it is

TABLE 2. Ni Speciation for Industrial Facilities Discharging to the SJSC WPCP

facility	$[Ni]_{diss}$ (nM)	$[NiL_1]$ (nM)	$[NiEDTA^{2-}]$ (nM)	$[EDTA]$ (nM)	$[NiL_1]/[Ni]_{diss}$ (%)	$[NiEDTA^{2-}]/[Ni]_{diss}$ (%)	$[NiEDTA^{2-}]/[NiL_1]$ (%)
hard drive manufacturers							
1	3400	1700	1650	2400	50	48	97
2	8900	3100	2650	NM[a]	35	30	85
3	560	430	NM	280	77	NM	NM
printed circuit boards							
1	130	120	135	10000	92	104	113
2	240	240	NM	NM	100	NM	NM
3	600	570	620	>50000	95	103	109
metal finishers							
1	14800	7400	NM	NM	50	NM	NM
miscellaneous operations							
1	140	105	NM	NM	75	NM	NM

[a] NM, not measured.

present in domestic wastewater. The difference between $[NiEDTA^{2-}]$ observed at the plants that receive substantial industrial discharges and at the plants that receive little industrial discharge suggests that industrial sources account for approximately half of the $NiEDTA^{2-}$ in wastewater effluent. In San Jose, the location of the facility with the highest $[NiEDTA^{2-}]$, our results indicate that industrial wastewater contains relatively high concentrations of $NiEDTA^{2-}$ and other EDTA complexes.

Assuming that the speciation of Ni in an industrial sample is representative of the industry sampled (e.g., the speciation of Ni from all hard drive manufacturers is similar), data on $[Ni]_{tot}$ and the volume of wastewater discharged (*37*) can be used to estimate $NiEDTA^{2-}$ contributions from each industry. This crude analysis indicates that ~50 nM of the strongly complexed Ni at the SJSC facility is attributable to industrial sources, which is consistent with the difference in NiL_1 observed between the WPCPs that receive industrial discharge and those that receive only domestic wastewater. In addition to the large amounts of $NiEDTA^{2-}$ discharged by many industries, some industries, particularly printed circuit board manufacturing, discharge relatively high concentrations of EDTA complexes other than $NiEDTA^{2-}$ (Table 2).

The observation that $NiEDTA^{2-}$ accounts for all of the strongly complexed Ni measured in industrial wastewater is consistent with reported industrial uses. On a mass basis, EDTA accounts for 85% of the aminocarboxylates, which are the most common synthetic chelating agents (*21*). Even if compounds other than EDTA are discharged by some industries, it is unlikely that they would be present in wastewater effluent at significant concentrations, because most chelating agents are substantially removed during wastewater treatment (*17, 20*).

WPCPs that do not receive significant industrial discharges (i.e., DSR and MVSD) must receive $NiEDTA^{2-}$ from another source. There are a number of possible domestic sources of EDTA. For example, EDTA is present in many household products, including soaps and household cleaning agents, and is used as an additive for food products to prevent trace-metal-catalyzed oxidation (*38*). The Na_4EDTA used in these products is quickly converted to other metal−EDTA complexes upon exposure to trace metals in the wastewater collection system, and the formation of $NiEDTA^{2-}$ is thermodynamically favored under conditions encountered in wastewater.

Ligand Fate. Seasonal differences in dissolved Ni speciation in South San Francisco Bay (Figure 3) are related to differences in Ni speciation between the two major anthropogenic sources of Ni: wastewater effluent and surface runoff (*16*). In January, when surface runoff and wastewater each contribute approximately equal amounts of freshwater to South San Francisco Bay (*39*), $[NiL_1]$ is less than < ~25 nM and accounts for less than half of $[Ni]_{diss}$. In April and July, when surface runoff decreases, $[NiL_1]$ in the low-salinity South Bay water increases to as much as 110 nM as wastewater effluent becomes the dominant source of freshwater.

The relationship between salinity and concentration can be used to assess the sources and sinks of the different Ni species, because salinity is a surrogate for the mixing of freshwater (i.e., wastewater effluent and surface runoff) with seawater (*27*). Knowing that the strongly complexed Ni in low-salinity water is $NiEDTA^{2-}$, we can predict its fate in San Francisco Bay. Dissociation of the complex is unlikely because the rate of dissociation of the $NiEDTA^{2-}$ complex is slow (*24−26*) relative to the residence time of the complex in the bay. Sorption of $NiEDTA^{2-}$ also is unlikely under the conditions found in San Francisco Bay (*40−43*). Therefore, one would expect conservative behavior of NiL_1 within the bay.

The Ni speciation data collected in San Francisco Bay support the hypothesis that NiL_1 behaves conservatively. Despite scatter in the data, which is to be expected for spatially varied samples collected over a period of several days in an estuarine system, it is evident that $[NiL_1]$ is greater at low salinity and decreases as salinity increases, particularly during July and April. In contrast, no clear relationship is evident between other Ni species (i.e., Ni' and NiL_2) and salinity. This implies that sources and sinks of weaker Ni complexes (e.g., sediments) are important in San Francisco Bay. This behavior is consistent with previous work in the Tamar estuary (*33*).

Our results have important implications for the speciation of Ni and other metals in estuarine systems. As mentioned previously, significant concentrations of strongly complexed Ni have been observed in many estuarine systems. All of the estuaries studied receive some wastewater effluent, and as we have demonstrated, wastewater effluent usually contains $NiEDTA^{2-}$. Therefore, it would be prudent to consider the possibility that $NiEDTA^{2-}$ could be the strongly complexed Ni species observed in wastewater-influenced estuarine waters.

Our data indicate that Ni and Fe complexes generally account for <25% of the EDTA in wastewater effluent. Equilibrium speciation calculations (*44*) indicate that a significant fraction of the pollutant metals [i.e., Cu(II), Zn(II), Pb(II)] discharged by WPCPs also could be complexed by EDTA (assumed conditions: $[Cl^-] = 5.7$ mM, $[SO_4^{2-}] = 2.8$ mM, $[CO_3^{2-}]_{tot} = 2$ mM, $[PO_4^{3-}]_{tot} = 0.3$ mM, $[NO_3^-] = 0.3$ mM; pH 8). We predict that some of the metal−EDTA complexes (e.g., Pb, Zn) will be converted to chloro complexes when mixed with seawater (assumed conditions: $[Cl^-] = 550$ mM, $[SO_4^{2-}] = 30$ mM, $[CO_3^{2-}]_{tot} = 2$ mM; pH 8). This raises the possibility that certain metals could pass through WPCPs in unreactive forms that dissociate into more

bioavailable and potentially toxic forms when mixed with seawater. Future work should focus on the measurement of other metal−EDTA complexes in wastewater effluents and the possibility that certain metal−EDTA complexes may undergo dissociation after discharge.

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