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Copper and Nickel Partitioning with Nanoscale Goethite

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COPPER AND NICKEL
PARTITIONING WITH NANOSCALE GOETHITE

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By

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I HEREBY RECOMMEND THAT THE THESIS PREPARED UNDER MY
SUPERVISION BY Kelsey Marie Danner ENTITLED Copper and Nickel Partitioning
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ABSTRACT

Danner, Kelsey M. M.S. Department of Earth and Environmental Sciences, Wright State University, 2013. Copper and nickel partitioning with nanoscale goethite.

Goethite is an ideal sorbent for investigations of metal partitioning with iron oxyhydroxides because it is the most abundant iron oxyhydroxide in sediments (Langmuir, 1997; van der Zee et al., 2003), and cations have a strong affinity for goethite (Coughlin and Stone, 1995). Steady-state partitioning of nickel (Ni) and copper (Cu) to nanoscale goethite (α-FeOOH) was investigated experimentally under conditions intended to be representative of those in natural waters. Manipulated conditions included i) sorbent mass, ii) solute metal concentration, iii) reaction time, iv) pH, v) ionic strength (I), and vi) humate concentration (competitive ligand) to examine how these factors influenced the partitioning of Cu and Ni between water and goethite. This work suggests that solute adsorption in natural systems is determined by ambient pH and available competitive ligands. Distribution coefficients widely increased as solution pH was raised above the point of zero net proton charge (PZNPC) of goethite. As humate concentration was increased, a significant decrease in distribution coefficients was observed. Ionic strength had no observed effect on solute adsorption. Increasing reaction time did not increase solute adsorption, which suggests that all possible adsorption occurs within 24 hours of solute introduction. The distribution coefficients for Ni and Cu obtained in this

study fall within and above reported ranges for soil/water, suspended matter/water, and sediment/water interfaces. Because K_D values from this study are within and above the reported range, goethite may significantly contribute to the adsorption of both Ni and Cu. This study warrants further investigation of metal partitioning to nanoscale goethite within natural surface and pore water to determine its potential significance.

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I.   INTRODUCTION

The bioavailability of trace metals in sediments is influenced by their affinity for solid-phase sulfides, organic carbon, and iron (Fe) and manganese oxides (Lion et al., 1982; Benoit et al., 1994; Hammerschmidt and Fitzgerald, 2004; Jeong et al., 2007; Costello et al., 2012), as well as speciation with dissolved organic and inorganic ligands (Tessier and Campbell, 1987; Allen and Hansen, 1996). Trace metals adsorb to iron oxides (Amacher et al., 1986; Grossl et al., 1994; Coughlin and Stone, 1995; Ford et al., 1997; Trivedi and Axe, 2001), and partitioning of metals with iron oxides in sediments can influence metal toxicity (Costello et al., 2011; Costello et al., 2012). The current procedure for estimating metal bioavailability and toxicity in sediments is the equilibrium partitioning (EqP) approach for metals developed by the U.S. Environmental Protection Agency (2005b). The EqP approach includes acidifying sediments and determining concentrations of acid volatile sulfides (AVS) and simultaneously extracted metal (SEM). Sulfide complexes and reduces the toxicity of many metals in sediments (Morris and Luther, 1999); however, organic carbon, Fe oxides, and manganese oxides also potentially reduce metal bioavailability when SEM concentrations are greater than those of AVS (Costello et al., 2012). While the EqP approach is useful for predicting nontoxic thresholds under reducing conditions, there is uncertainty in the method due to unaccounted binding by ligands such as Fe oxides (Costello et al., 2012). This work aims to model partitioning of nickel (Ni) and copper (Cu) with naturally occurring Fe oxides in

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aquatic sediments. Specifically, adsorption isotherms will be prepared with Ni and Cu as the solutes and nanoscale goethite (α-FeOOH) as the sorbent.

Goethite is an ideal sorbent for investigations of metal partitioning with iron oxyhydroxides because it is the most abundant iron oxyhydroxide in sediments (Langmuir, 1997; van der Zee et al., 2003), and cations have a strong affinity for goethite (Coughlin and Stone, 1995). Small diameter particles, such as natural goethite (surface area = $45-169$ m^2g^{-1}; Catts, 1982), have a relatively greater surface area:volume ratio, which, under the appropriate pH conditions, can result in a significant quantity of unsatisfied surface charge (Langmuir, 1997). At natural pH values, the partitioning of trace metals to iron oxyhydroxides is potentially significant and should therefore be further investigated. Surfaces of minerals are uncharged when the pH of surrounding water is equal to the point of zero net proton charge (PZNPC). The PZNPC for goethite is between 5.9 and 6.7 (Langmuir, 1997). When pH is greater than the PZNPC, iron oxyhydroxides have net negative surface charge (surface-site density = $2.6-16.8$ nm^{-2}; Davis and Kent, 1990) and exhibit cation exchange capacity (CEC). However, surface charge of iron oxyhydroxides is pH dependent and net positive below the PZNPC. Even when the pH is less than the PZNPC, negatively charged binding sites on the mineral surface remain and trace metal partitioning can occur. At pH 7, the CEC of iron oxyhydroxides ranges between $100-740$ meq per 100 g of material (Langmuir, 1997). Hydroxide groups are hypothesized to be the dominant surface ligand for CEC on goethite (Parfitt et al., 1976; Parfitt and Russell, 1977).

The adsorption of ions by goethite has been examined experimentally, but not with conditions that mimic natural aquatic environments. Partitioning of anions (sulfate, selenite, oxalate, and phosphate) to goethite has been studied in an attempt to determine the complexes formed during adsorption (Parfitt and Russell, 1977; Anderson et al., 1985). Divalent anions were observed to form binuclear bridging complexes with goethite when two surface hydroxide groups were replaced with two oxygen atoms from a ligand (Parfitt and Russell, 1977). The study of phosphate adsorption on goethite showed enhanced particle aggregation with increased ligand loading, which subsequently led to slower adsorption kinetics (Anderson et al., 1985). Others have investigated the adsorption of divalent metals, such as manganese, cobalt, nickel, copper, lead, cadmium, and zinc (Grossl et al., 1994; Coughlin and Stone, 1995; Davis and Upadhyaya, 1996; Trivedi and Axe, 2001). The rate of divalent metal adsorption to goethite appears to be related to the removal of a water molecule from the primary hydration sphere of the cation (Grossl et al., 1994). Metals are observed to bind to goethite through either inner- or outer-sphere surface complexes, with inner-sphere binding being more prominent and stable due to direct cation binding with surface groups (Grossl et al., 1994). In contrast, outer-sphere binding occurs by coordinated water being positioned between a cation and the goethite surface group (Grossl et al., 1994). Coughlin and Stone (1995) studied competition between cations for goethite adsorption sites. Their work also examined nonreversible metal adsorption involving picolinic acid and a pH range of 3–8, all at an ionic strength of 10 mM. This study strives to create experimental conditions that more

closely mimic the natural environment by using humate, which is an abundant and environmentally significant ligand in natural waters (Kinniburgh et al., 1996; Milne et al., 2003), as a competitive ligand and keeping ionic strength at 1 mM, which is within the range of most freshwaters (U.S. EPA, 2012).

II.   METHODS

Steady-state partitioning of Cu and Ni to goethite was investigated experimentally under conditions intended to be representative of those in natural waters. I experimentally manipulated i) sorbent mass, ii) solute metal concentration, iii) reaction time, iv) pH, v) ionic strength (I), and vi) humate concentration (competitive ligand) to examine how these factors influenced the partitioning of Cu and Ni between water and goethite.

Chemicals and Supplies

Nanoscale goethite rods (50–150 nm diameter, 400–1000 nm length; Nanostructured & Amorphous Materials, Houston, TX) were cleaned prior to use by immersing in reagent-grade water (resistivity > 18.2 MΩ-cm), shaking for 12 h at 150 rpm, and then drying at 60 °C for 24 h. Heating goethite at low temperatures (60–90 °C) does not affect its structure or formation (Koch et al., 1986; Waychunas et al., 2005). Cleaned goethite was analyzed for "native" Ni and Cu in the mineral matrix so as to differentiate adsorbed metal from that in the mineral lattice. Stock solutions of Ni and Cu were prepared by dissolving $NiCl_2 \bullet 6H_2O$ and $CuCl_2 \bullet 2H_2O$ (ACS grade) in reagent-grade water and titrating pH to neutrality with NaOH (ACS grade). Reagent-grade water was used as a matrix for all experiments and ionic strength was manipulated with either KCl or $CaCl_2$ (ACS grade). Solution pH was adjusted with dilute HCl (J.T. Baker Instra-

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Analyzed) and NaOH (ACS grade). Sodium humate (Aldrich, Milwaukee, WI) was used for competitive ligand tests with goethite.

Experimental Batches

Partitioning of Cu and Ni with goethite was investigated under a variety of conditions by reacting dissolved metals in 10 mL of water with a known mass of goethite in 15-mL polypropylene centrifuge tubes (Tables 1 and 2). Four replicates tubes were prepared for each experimental treatment: three for analysis of metal in water and adsorbed to goethite and one for determining initial and final pH. pH was measured with a meter that was calibrated before each use with standards traceable to the U.S. National Institute of Standards and Technology (NIST). Goethite was weighed accurately (± 0.01 mg) into each tube so that specific masses could be used for calculation of distribution coefficients (K_D, L kg^{-1}). Each tube had a total solution volume of 10 mL that included reagent-grade water, metal standard, KCl solution, and in some cases, dilute solutions of HCl, NaOH, and humate. Samples were allowed to react for a prescribed time on a shaker table (150 rpm) at 25.0 ± 0.1 °C.

Reactions were terminated by separating the aqueous and goethite phases. Reaction tubes were centrifuged at 2500 rpm for 10 min. Supernatant was decanted into 12-mL syringes fitted with luer-lock polycarbonate syringe filter holders (25 mm; Sartorius, Bohemia, NY), holding either hydrophilic polycarbonate membranes (0.01 μm) or polyethersulfone membranes (0.03 μm; both filter types from Sterlitech Corporation,

Kent, WA), and filtered into a different tube. The nominal pore sizes of both filter types were sufficiently small to retain and separate the nanoscale goethite (> 0.05 μm diameter, > 0.4 μm length) from the filtrate. Syringes, filter holders, filters, and sample tubes were cleaned with HCl and rinsed with reagent-grade water prior to use. The goethite pellet and sample filter (removed from holder) were dissolved with 10 mL of 1 N HNO_3 (J.T. Baker Instra-Analyzed) and stored for analysis of adsorbed metal, whereas the filtrate was acidified to 2% with HNO_3 and analyzed for metal remaining in solution.

Determination of Nickel and Copper

Nickel and copper in dissolved goethite (i.e., adsorbed) and filtered water (solute) were determined by inductively coupled plasma mass spectrometry (ICP-MS; U.S. Environmental Protection Agency, 2007) with a PerkinElmer Elan 9000. Sample metal concentrations were measured after calibration with standard solutions traceable to the U.S. NIST. Quality control analyses included procedural and filtration blanks and replicate samples. Limits of quantification (APHA et al., 1995) were less than sample concentrations. Distribution coefficients (K_D, L kg^{-1}) of Cu and Ni between water and goethite were calculated according to the following equation:

$$K_D = Q/C \qquad \text{[Eq. 1]}$$

where Q was the concentration of metal sorbed to goethite (mol kg^{-1}) and C was the solute metal concentration after reaction (mol L^{-1}).

Analysis of Total Iron

Total iron was measured in selected samples of filtered water ($n = 65$) to confirm that little goethite either dissolved during the reactions or passed in colloidal form through membranes. Aliquots of water were oxidized with BrCl solution for > 1 h (Bloom and Crecelius, 1983), reduced with NH_2OH (12% wt:vol, ACS grade) to transform all Fe to Fe^{2+}, pH adjusted to 5 with 2 M acetate buffer (ACS grade), and reacted with phenanthroline to form a light absorbing complex (modified from Standard Method 3500-Fe D; APHA et al., 1995). Light absorbance of samples and procedural Fe standards was measured at 510 nm with a UV-Vis spectrophotometer. No colloidal or dissolved iron was detected in any of the filtrates; the method detection limit was 8.1 µM.

Table 1. Conditions of experimental batches with Ni as the solute. Experimental conditions were with 5 mg goethite in 10 mL of solution ($I = 1$ mM) for 1 d with no humate, except as described differently in the table.

Batch	Ni (nM)	Variable	Final pH
1	1000	*Goethite mass (mg)* = 5, 10, 100, 500, 1000	6.1–10.3
2	varied	*Metal concentration (nM)* = 1, 10, 50, 100, 500, 1000, 5000, 10000, 50000, 100000, 500000, 2500000	6.8–9.4
3	500, 5000	*Reaction time (days)* = 0.08, 1, 2, 4, 6, 10, 13, 16, 20	6.6–8.5
4	1000	*pH* = 4, 5, 6, 7, 8, 9, 10	4.3–9.6
5	1000	*Ionic strength (mM)* KCl = 0.02, 0.1, 1, 10, 50, 250, 1000 CaCl$_2$ = 0.1	8.2–8.8
6	1000	*Humate (mM)*[a] = 0.055, 0.55, 5.5, 55	7.4–10.0

[a] Molar concentrations of humate were estimated assuming that 1 mole of Aldrich humatic acid was 1630 g (Chin et al., 1997).

Table 2. Conditions of experimental batches with Cu as the solute. Experimental

conditions were with 5 mg goethite in 10 mL of solution (I = 1 mM) for 1 d with no

humate, except as described differently in the table.

Batch	Cu (nM)	Variable	Final pH
1	10000	*Goethite mass (mg)* = 5, 10, 100, 500, 1000	9.6–10.4
2	varied	*Metal concentration (nM)* = 1, 10, 50, 100, 500, 1000, 5000, 10000, 50000, 250000	5.8–8.9
3	5000, 50000	*Reaction time (days)* = 0.8, 1, 2, 4, 6, 10, 13, 16, 20	5.9–7.4
4	10000	*pH* = 4, 5, 6, 7, 8, 9, 10	4.3–9.9
5	10000	*Ionic strength (mM)* KCl = 0.02, 0.1, 1, 10, 50, 250, 1000 CaCl$_2$ = 0.1, 250	6.4–7.1
6	10000	*Humate (mM)*[a] = 0.055, 0.55, 5.5, 55, 550	7.3–10.0

[a] Molar concentrations of humate were estimated assuming that 1 mole of Aldrich

humatic acid was 1630 g (Chin et al., 1997).

III.   RESULTS AND DISCUSSION

Effect of Sorbent Mass

Adsorption of Ni and Cu by goethite was initially investigated by reacting the same initial concentration of solute Ni (1000 nM) and Cu (10000 nM) with varying masses of sorbent (5 to 1000 mg). Distribution coefficients of both Ni and Cu were comparable between 5 and 10 mg of goethite and decreased exponentially with greater masses of sorbent (Figure 1). The decrease of K_D with sorbent mass greater than 10 mg was an artifact of the distribution coefficient calculation. Greater than 99.5% of the initial metal concentration was adsorbed to goethite at goethite masses between 10 and 1000 mg (Figure A1), indicating that Cu and Ni did not have a lower affinity for the sorbent at greater masses. Instead, increasing sorbent masses between 10 and 1000 mg decreased the mass-normalized sorbed metal concentration (mol/kg; i.e., increase of denominator) and resulted in a proportional decrease in calculated K_D values.

Figure 1. Distribution coefficients ($K_D \pm 1$ SD) of Cu and Ni as a function of goethite mass (5−1000 mg) at constant initial concentrations of solute metal (1000 nM Ni, 10000 nM Cu), pH = 8−10, and ionic strength (1 mM).
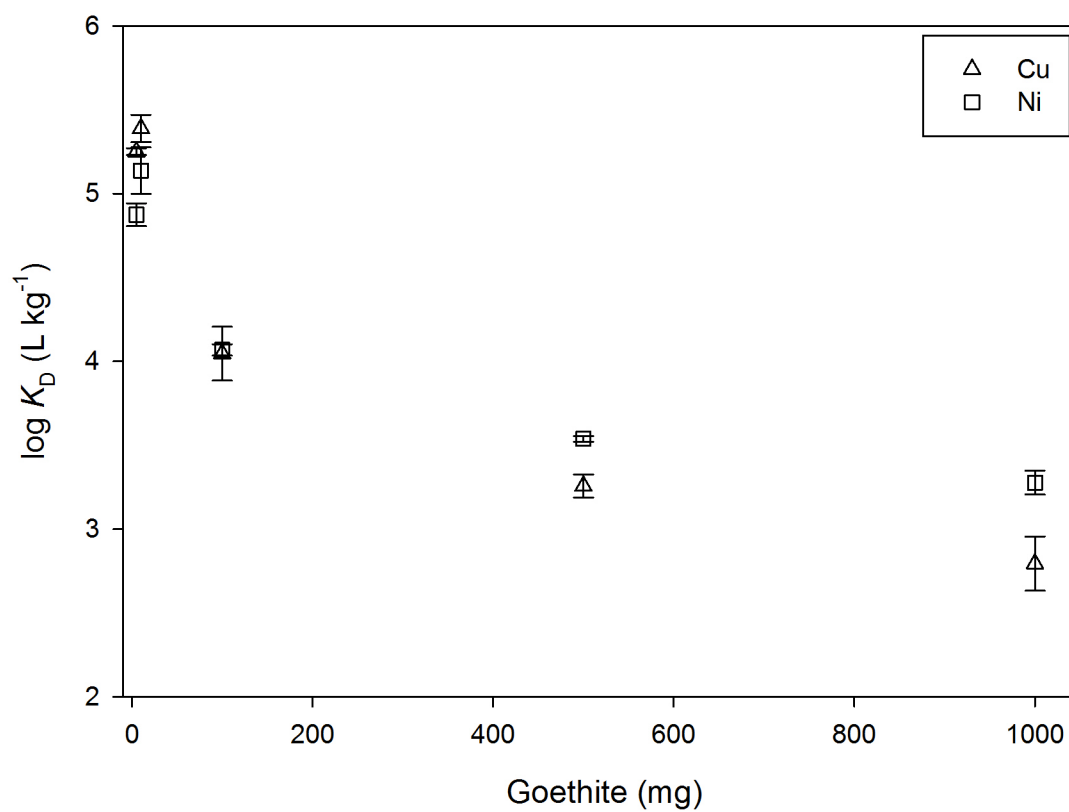
Effect of Solute Concentration

Solute concentration isotherms were produced to estimate the break-through concentration of Cu and Ni with goethite (5 mg). Metal concentrations utilized for these tests ranged from 1 nm to 2.5 µM of Ni and from 1 nm to 0.25 µM of Cu. For both Cu and Ni, K_D increased with initial solute concentrations up to 5000 nM, which was determined to be the break-through concentration, and then decreased with greater concentrations (Figure 2). The distribution coefficient increased as the initial metal concentrations increased from 1 to 5000 nM because the adsorption capacity of goethite had not been reached. Beyond the break-through concentration, the amount of adsorbed metal continued to increase (Figure 3), but the increase was disproportional to the greater increase of solute metal, resulting in decreased K_D values. Accordingly, it appears that goethite has more than one adsorption mechanism for Cu and Ni.   Initial adsorption of Cu and Ni is likely due to the net negative surface charge of goethite and complexation with anionic ligands. After these binding sites are titrated, the adsorption mechanism likely switches from inner- to outer-sphere binding, which occurs due to weaker electrostatic forces and can include a water molecule between the metal and sorbent surface (Grossl et al., 1994; Waychunas et al., 2005). Inner-sphere binding is more stable because the metal binds directly with surface groups and there are no coordinated waters present that weaken the bond (Grossl et al., 1994). It is likely that outer-sphere binding becomes the dominant binding type after the break-through concentration; accordingly,

subsequent adsorption that occurs after the break-through concentration is either not as strong or there are fewer sites outer- than inner-sphere bonding sites.

Adsorption capacity of nanoscale goethite for Cu and Ni was estimated for both metals at their break-through concentration (5000 nM) and the maximum test concentration. Adsorption capacity (atoms nm^{-2}) of nanoscale goethite was determined from adsorbed Ni and Cu concentrations according to the following equation:

$$\text{Adsorption capacity} = \frac{Me_{ads}}{goethite} \times SSA_{goethite} \times \frac{6.022 \times 10^{23} \text{ atoms}}{\text{mole Me}} \qquad \text{[Eq. 2]}$$

where Me_{ads} is the amount of metal adsorbed (mol), $goethite$ is the mass of goethite sorbent (g), and $SSA_{goethite}$ is the specific surface area of goethite ($4-6 \times 10^{19}$ nm^2 g^{-1}; Nanostructured & Amorphous Materials, Inc.). The adsorption capacity of goethite with 5000 nM ranged $0.07-0.12$ atoms nm^{-2} for Cu and $0.07-0.14$ atoms nm^{-2} for Ni. Adsorption capacities were estimated similarly for the highest metal concentrations tested. The adsorption capacity of goethite with 250,000 nM Cu ranged from 1.1 to 1.7 Cu atoms nm^{-2}. Adsorption capacity of goethite with 2,500,00 nM Ni ranged from 1.7 to 3.3 Ni atoms nm^{-2}. The range of adsorption capacities for nanoscale goethite estimated from this study was in good agreement with an adsorption capacity of 1.1 Cu atoms nm^{-2} determined for micron-scale goethite (Coughlin and Stone, 1995). Hayes (1987) reported an experimental adsorption capacity of 2.6 atoms nm^{-2} and modeled adsorption capacity of 7.0 atoms nm^{-2} for Pb^{2+} partitioning to goethite.

Figure 2. Distribution coefficients ($K_D \pm 1$ SD) of Cu and Ni as a function of solute metal concentration (10 nM–2.5 µM) at constant goethite mass (5 mg), pH = 7−9, and ionic strength (1 mM).
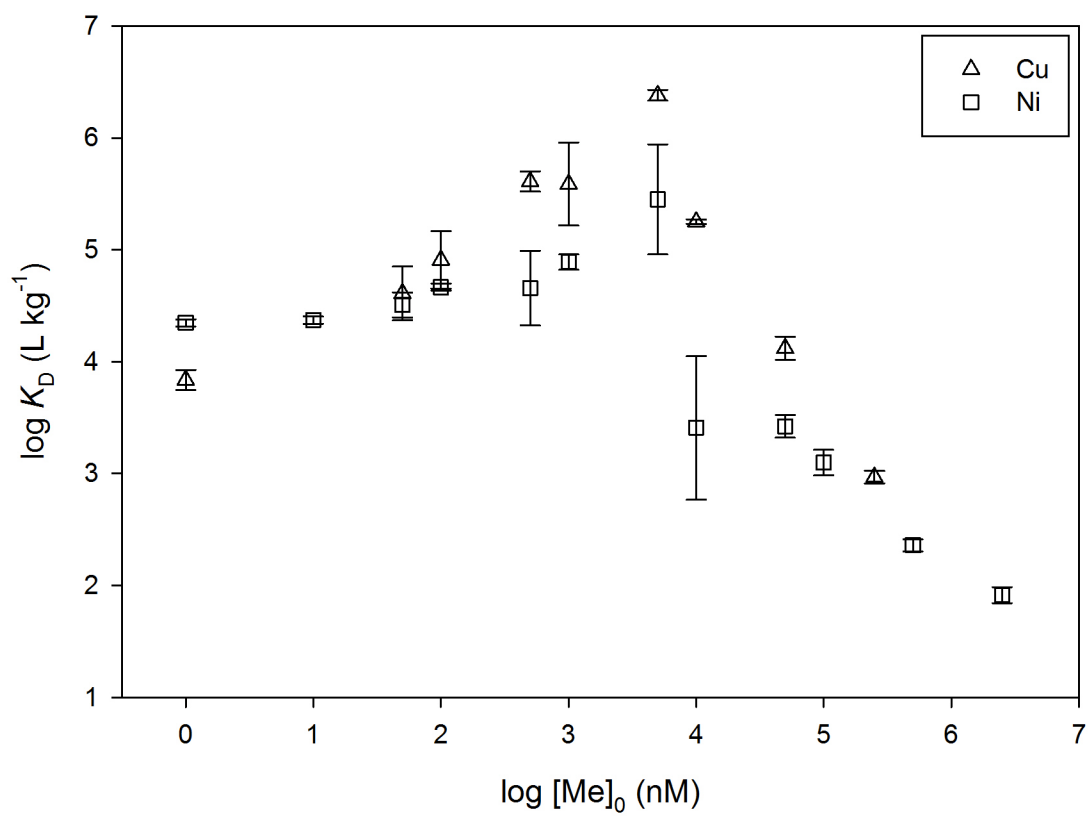
Figure 3. Adsorbed amount ($Q \pm 1$ SD) of Cu and Ni as a function of initial solute metal concentration (10 nM–2.5 µM) at constant goethite mass (5 mg), pH = 7−9, and ionic strength of 1 mM.
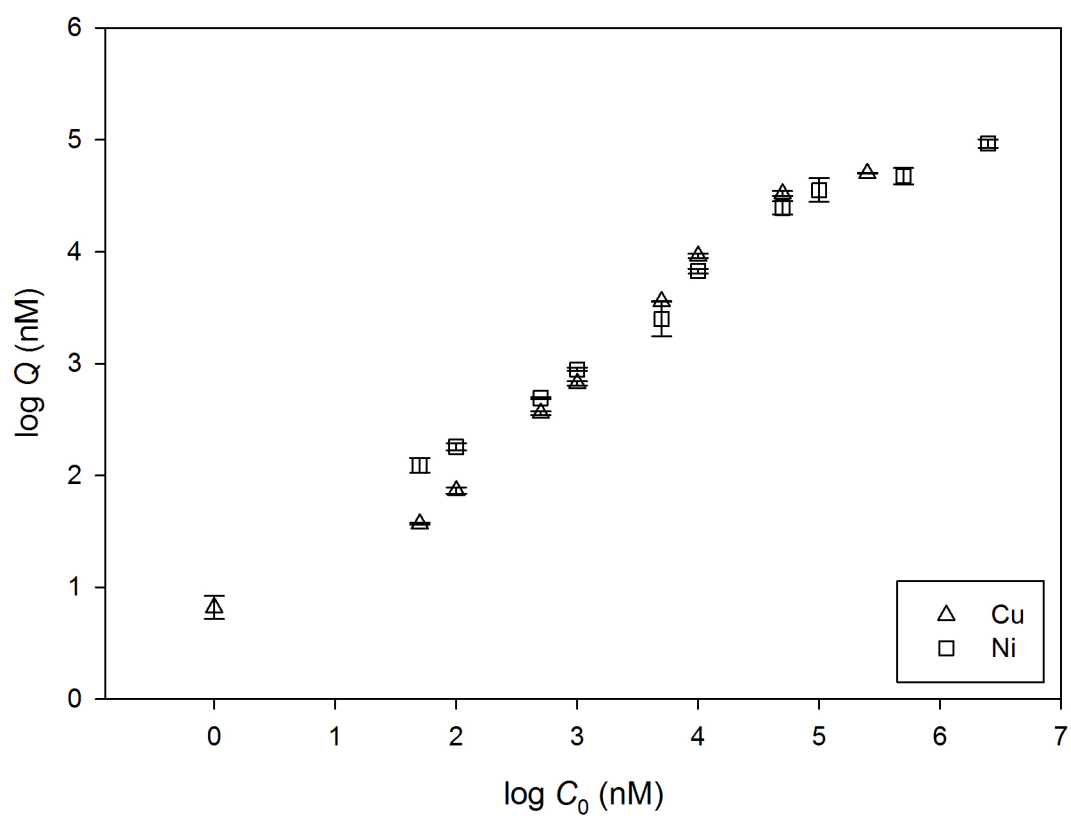
Effect of Reaction Time

The partitioning of Cu and Ni with goethite did not change appreciably over time. Distribution coefficients were determined for Cu and Ni at two different solute metal concentrations across a series of reaction periods from 2 h to 20 d with 5 mg of goethite (Figure 4). Low and high concentrations of Ni (500 and 5000 nM) resulted in K_D values that remained within the same order of magnitude (i.e., roughly the uncertainty of the measurements) throughout the 20-d period. Distribution coefficients for the low (5000 nM) and high (50000 nM) Cu treatments also were unchanged during the 20-d period. Lower partitioning coefficients for high Cu treatment were expected because 50000 nM is beyond the break-through concentration for Cu with goethite. These results suggest that steady-state partitioning of Ni and Cu was achieved within 1 d of reaction and that results from all other tests, which were conducted for only 1 d, are representative of steady state conditions.

Figure 4. Distribution coefficients ($K_D \pm 1$ SD) of Cu and Ni as a function of reaction time (2 h−20 d) at constant goethite mass (5 mg), pH = 6−9 and ionic strength (1 mM).
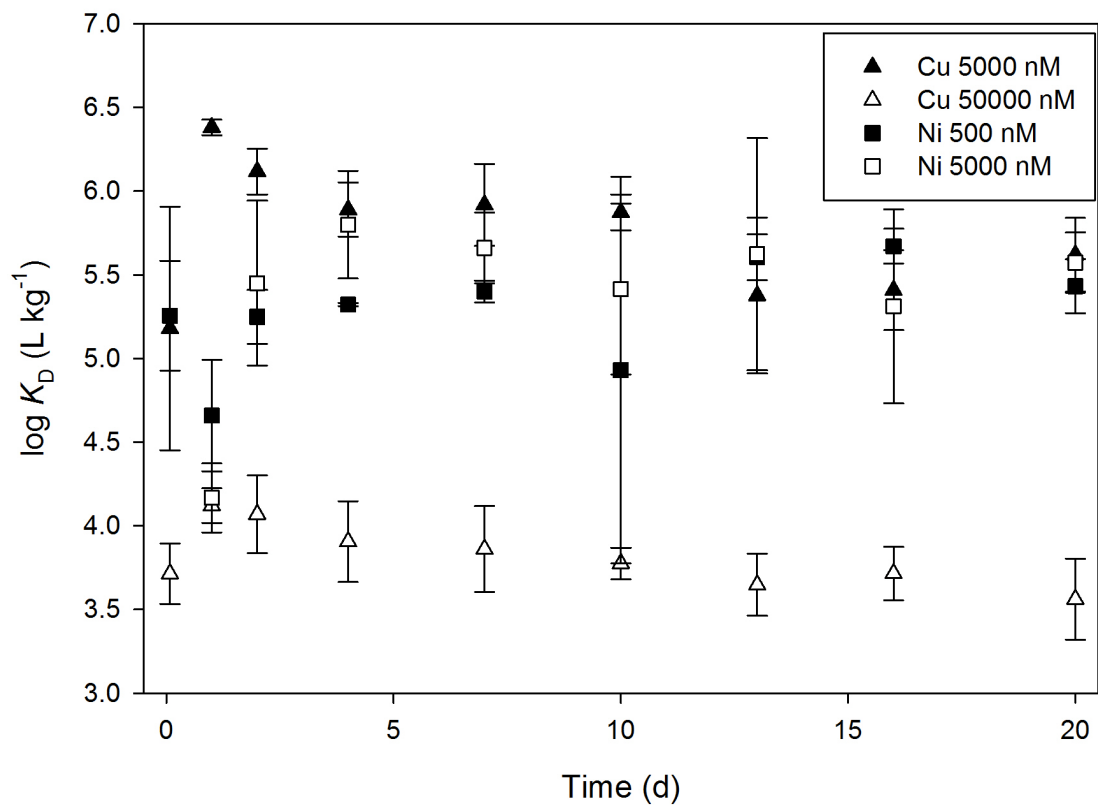
Effect of pH

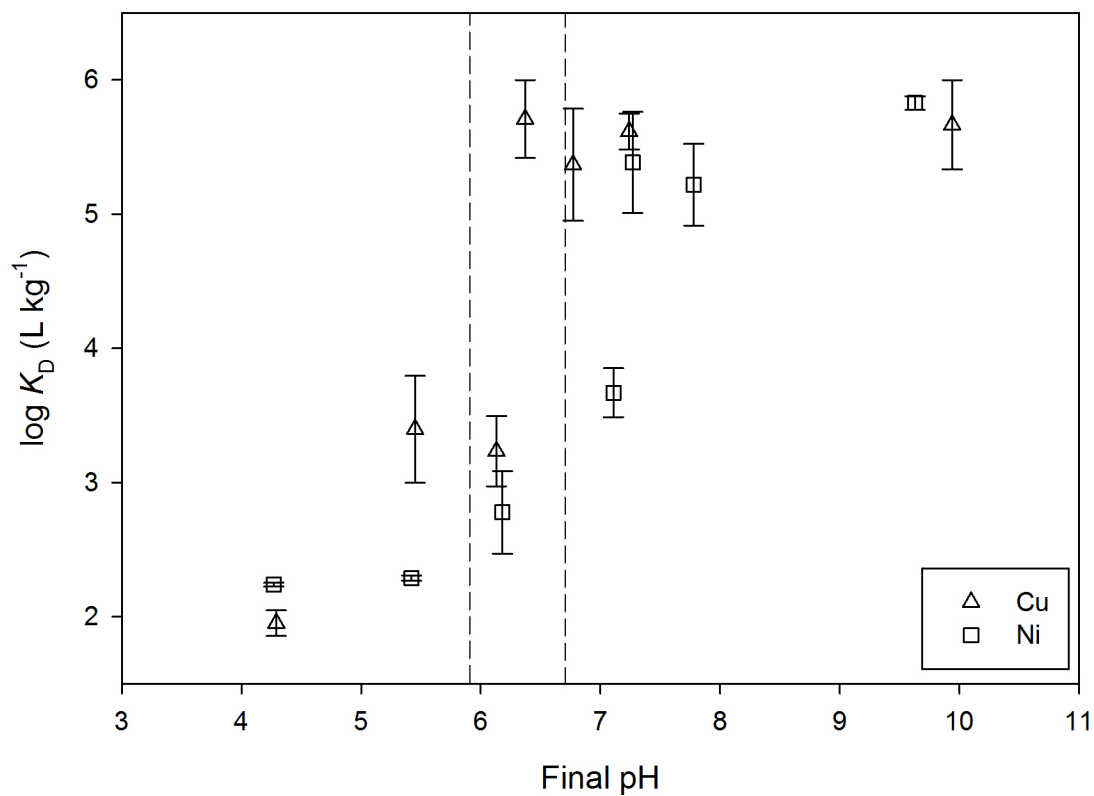Distribution coefficients of Cu and Ni varied as a function of pH and illustrated the adsorption edge of both metals to goethite (Figure 5). Adsorption tests were conducted with initial solution pH values ranging from 4 to 10, which bracket the PZNPC of goethite (5.9–6.7; Langmuir, 1997). Solution pH after the 1-d reaction differed by less than 0.5 units, on average, from initial conditions. pH changes during the reaction periods were a result of buffering by the goethite, which was kept to a minimum by using only 5 mg of the mineral per 10 mL of solution. Distribution coefficients of Cu and Ni were about 10^2 L kg^{-1} at pH 4.3 and increased exponentially to an asymptotic value of about $10^{5.5}$ L kg^{-1} when pH was greater than ~7.3 (log $K_{D\ Ni}$ = 0.877pH – 1.997, R^2 = 0.68; log $K_{D\ Cu}$ = 1.34pH – 3.882, R^2 = 0.80). The relationships between the distribution coefficients and pH for both metals are consistent with the surface charge of goethite being net positive and less attractive to either metal at pH values less than the PZNPC and greater adsorption when the surface is net negative at higher pH (Figures A3 and A4). Greater metal adsorption to goethite at higher pH also can be attributed to proportionally more of the Cu and Ni existing as the $CuOH^+$ and $NiOH^+$ species, which are the form of the metal that preferentially sorb to iron oxides (Rai et al., 1984).

Figure 5. Distribution coefficients ($K_D \pm 1$ SD) of Cu and Ni as a function of final pH with a constant goethite mass (5 mg), initial solute metal concentration (1000 nM Ni, 10000 nM Cu) and ionic strength (1 mM). The dashed lines indicate the PZNPC of goethite (5.9–6.7; Langmuir, 1997).

Effect of Ionic Strength

Ionic strengths ranging from those in dilute rainwater (0.02 mM) to that in excess of seawater (1000 mM) had no effect of the partitioning of either Ni or Cu to goethite (Figure 6). Distribution coefficients of both metals were unrelated to I when K^+ and Cl^- were the dominant ions in solution (Spearman, p-values > 0.3). However, when $CaCl_2$ was used to adjust I for Ni, the mean distribution coefficient of Ni was significantly less than when I was adjusted as a result of KCl (Mann-Whitney rank sum, $p < 0.001$). In contrast, the partitioning of Cu to goethite was not different whether KCl or $CaCl_2$ were used to adjust I to either 0.1 or 250 mM (Mann-Whitney rank sum, p-values > 0.05). The apparent difference of Ni partitioning with goethite whether Ca^{2+} or K^+ were in solution suggests that Ca^{2+} may compete with Ni^{2+} for available surface sites on goethite, although the concentration of Ca in solution was 10^5-fold greater than that of Ni. However, Ca had no significant effect on Cu partitioning with goethite (Mann-Whitney rank sum, p-values > 0.05). Differences in chloride ligand concentration had no effect on partitioning of either Cu or Ni, as evidenced by the K_D not changing with greater dissolved KCl (Figure 6). It was expected that increasing I, and subsequently chloride concentration, might decrease the adsorption of Ni and Cu by goethite due to competitive binding of the metals by chloride. Swallow et al. (1980) found that increasing I led to a decrease in lead adsorption to hydrous ferric oxide. Similar to the current study, however, Hayes and Leckie (1987) found that cadmium adsorption to goethite was not affected by I and could be modeled as an inner-sphere surface reaction. Nickel adsorption to

amorphous $Fe(OH)_3$ was unaffected by I (Green-Pedersen et al., 1997). Results from

tests examining Cu and Ni partitioning as a function of initial solute metal concentration

(Figure 2) suggest that the majority of Cu and Ni adsorption occurs due to inner-sphere

binding, which could explain why observed adsorption is not dependent on I throughout

the tested range.

Figure 6. Distribution coefficients ($K_D \pm 1$ SD) as a function of solution ionic strength (0.02–1000 mM) resulting almost entirely from addition of either KCl or $CaCl_2$ matrix modifiers at constant goethite mass (5 mg), initial solute metal concentration (1000 nM Ni, 10000 nM Cu), pH = 6−9, and ionic strength (1 mM).
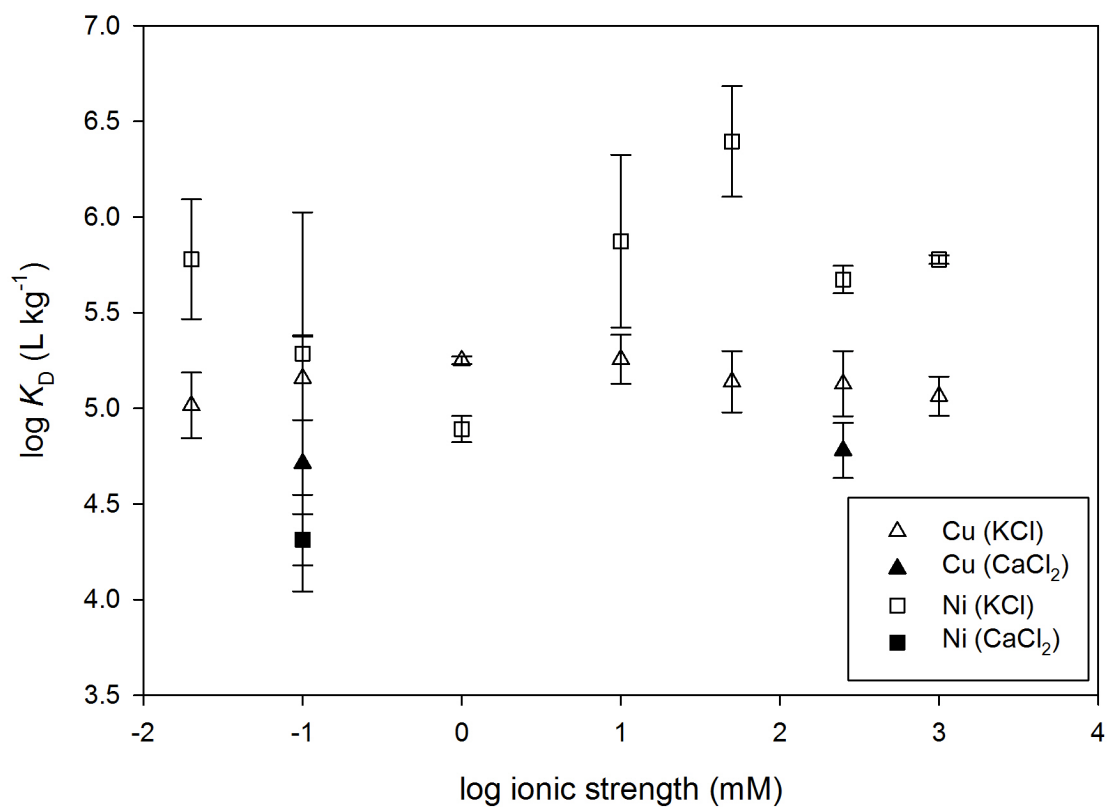
Effect of Humate Concentration

Addition of humate as a competitive ligand for complexing Cu and Ni in solution decreased adsorption of the metals to goethite (Figure 7). While a low concentration of humate (0.055 mM) had no effect on either Cu or Ni partitioning with goethite relative to tests without the ligand (Mann-Whitney rank sum, *p*-values > 0.7), greater concentrations, including those comparable to the dissolved organic contents of natural surface and pore waters (0.7−13 mg L^{-1}, Oliver et al., 1983), resulted in a substantial decrease of the K_D. These results are consistent with the known affinities of Ni (log K' = 3−6 at pH =7 and I = 200 mM; Glaus et al., 2000) and Cu (log K' = 5 at pH = 3.5; Pandey et al., 2000) for humate and show that dissolved organic ligands can attenuate the significance of goethite in binding Cu and Ni.

Metal availability is affected by dissolved organic and inorganic ligands (Allen and Hansen, 1996). These ligands have a wide range of surface chemical properties that allow for substantial metal adsorption (Lion et al., 1982). As dissolved ligand concentrations are increased, charged functional groups on these compounds (e.g., thiol and carboxyl groups) compete against the surface charge of goethite and reduce the amount of adsorbed metal. Alternatively, such ligands can adsorb to metal oxide surface and affect apparent metal partitioning by either complexing ions while bound to the surface or by physically blocking surface sites of the metal oxide (Schwertmann, 1991; Kim et al., 2004; Saito et al., 2005; Reiller et al., 2006). It is likely that humate inhibited adsorption of Cu and Ni to goethite by both complexing the metals in solution and by

blocking surface sites on goethite: at the highest concentration (550 mM), humate was visibly retained on filters in association with goethite. Metals are known to incorporate in ternary systems with goethite and humate (Saito et al., 2005). Though ternary binding was not measured in this study, it likely occurred as humate concentration was increased. However, this was not a significant source of metal adsorption because as humate concentrations increased, K_D values decreased. Therefore, this study suggests preferential binding of humate to goethite, rather than enhanced binding through a ternary system.

Figure 7. Distribution coefficients ($K_D \pm 1$ SD) of Cu and Ni as a function of nominal

humate concentration (0.055−550 mM) at constant goethite mass (5 mg), initial solute

metal concentration (1000 nM Ni, 10000 nM Cu), pH = 7−10, and ionic strength (1 mM).
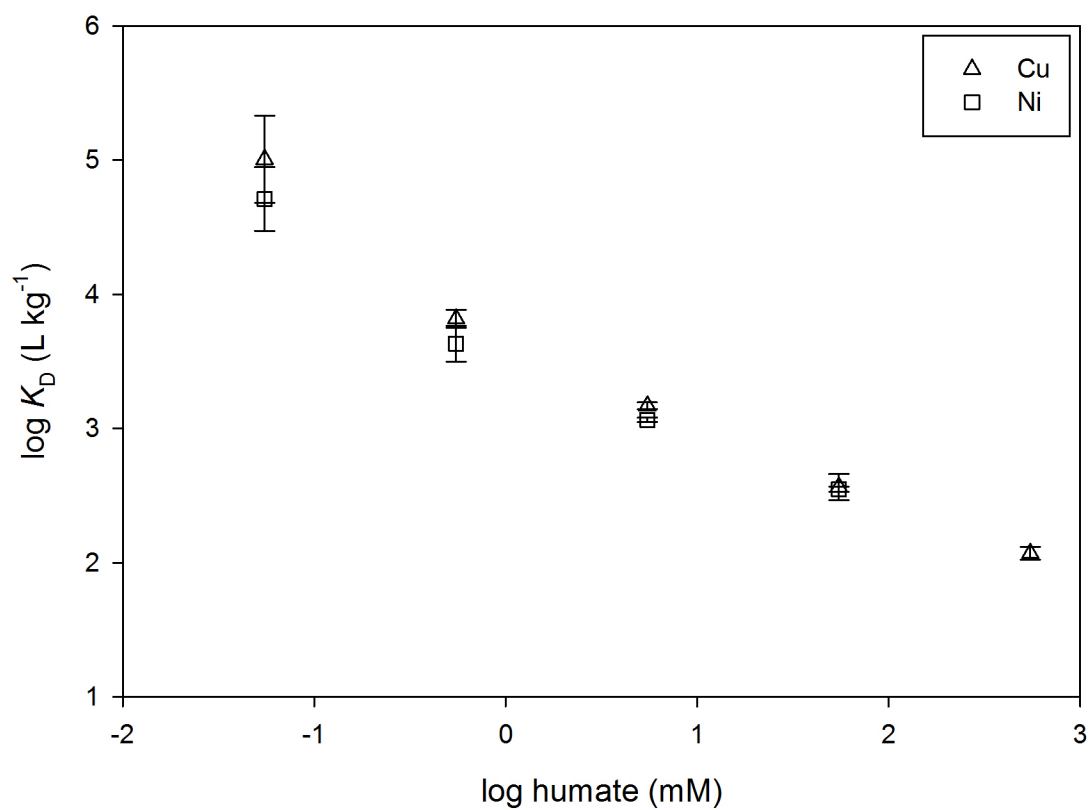
IV. CONCLUSION

Copper and nickel readily adsorb to nanoscale goethite. The greatest influences on solute adsorption were solution pH and competitive ligands. Distribution coefficients increased by about three orders of magnitude as solution pH was raised above the PZNPC of goethite. As humate concentration was increased, a significant decrease in distribution coefficients was observed. Ionic strength had no observed and consistent effect on Cu and Ni adsorption to goethite.

The environmentally realistic conditions examined in this work have given higher distribution coefficients than other studies. This work suggests that Ni and Cu adsorption to goethite in natural systems is determined by ambient pH and availability of competitive ligands. Metal adsorption to goethite will occur most prevalently in aquatic environments of neutral to alkaline pH with low organic carbon. In environments having pH less than neutral, such as many surface sediments, goethite will not likely be a primary solid-phase ligand for Ni and Cu, and by extension other transition metals, and sulfides and organic matter will be more significant. In addition to its effect on metal speciation as the free ion, low pH potentially exacerbates metal bioavailability and toxicity as a result of its control on complexing capacity of goethite.

The distribution coefficients for Ni and Cu determined in this study are comparable to, if not greater than, those reported for soil/water, suspended matter/water, and sediment/water interfaces. Median values of $\log K_D$ for Ni in the United States are 3.1, 4.6, and 4.0 L kg^{-1} for soil/water, suspended matter/water, and sediment/water,

respectively, under natural conditions (U.S. EPA, 2005a). The same nationwide review reports median log K_D values for Cu, under natural conditions, of 2.7, 4.7, and 4.2 L kg^{-1} for soil/water, suspended matter/water, and sediment/water, respectively. Because K_D values from this study are within and above the reported median values observed in natural systems, goethite may significantly contribute to the adsorption of both Ni and Cu to particles in the environment. The current approach for predicting nontoxic thresholds has uncertainty due to unaccounted binding by ligands other than sulfides and organic carbon such as iron oxides. When estimating metal bioavailability and toxicity, measurements of pH and dissolved organic carbon would aid in determining the potential for adsorption to iron oxides.

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VI. APPENDIX

**Figure A1.** Solution amount ($C \pm 1$ SD) of Cu and Ni relative to initial amount as a function of goethite mass (5–1000 mg) at constant initial solute concentration (1000 nM Ni, 10000 nM Cu), pH = 8−10, and ionic strength (1 mM).
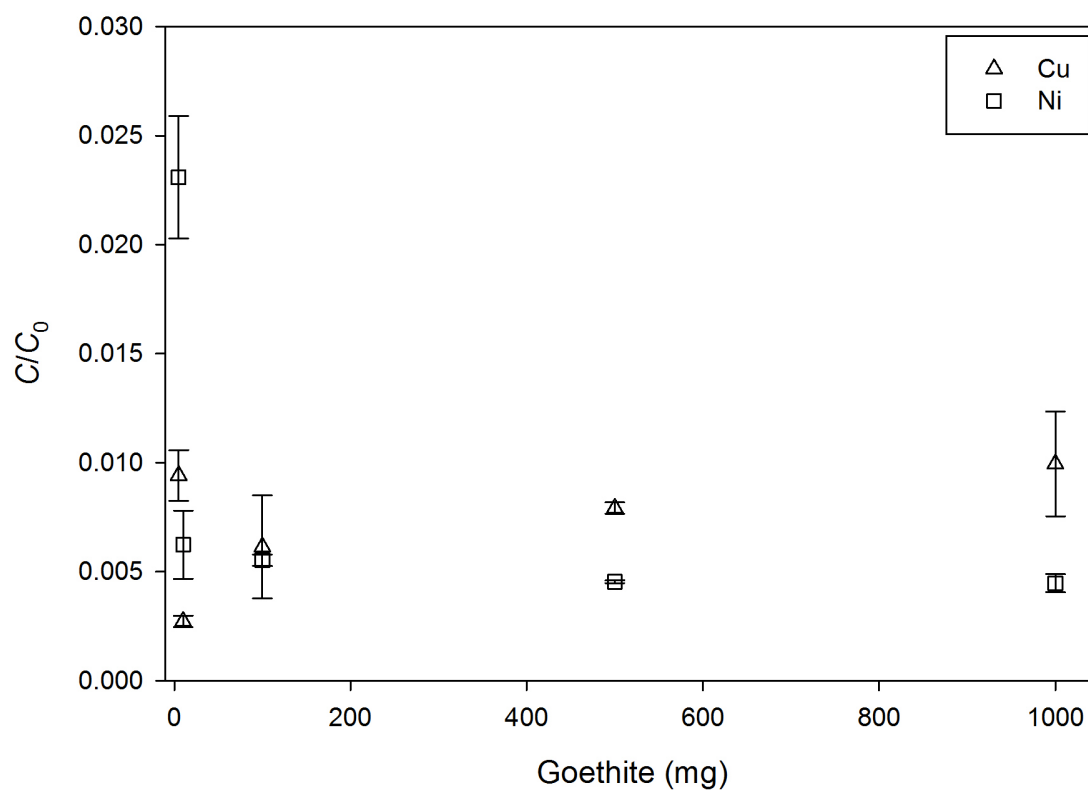
Figure A2. Adsorbed amount ($Q \pm 1$ SD) of Cu and Ni relative to initial solute amount as a function of goethite mass (5–1000 mg) at constant initial solute concentration (1000 nM Ni, 10000 nM Cu), pH = 8−10, and ionic strength (1 mM).
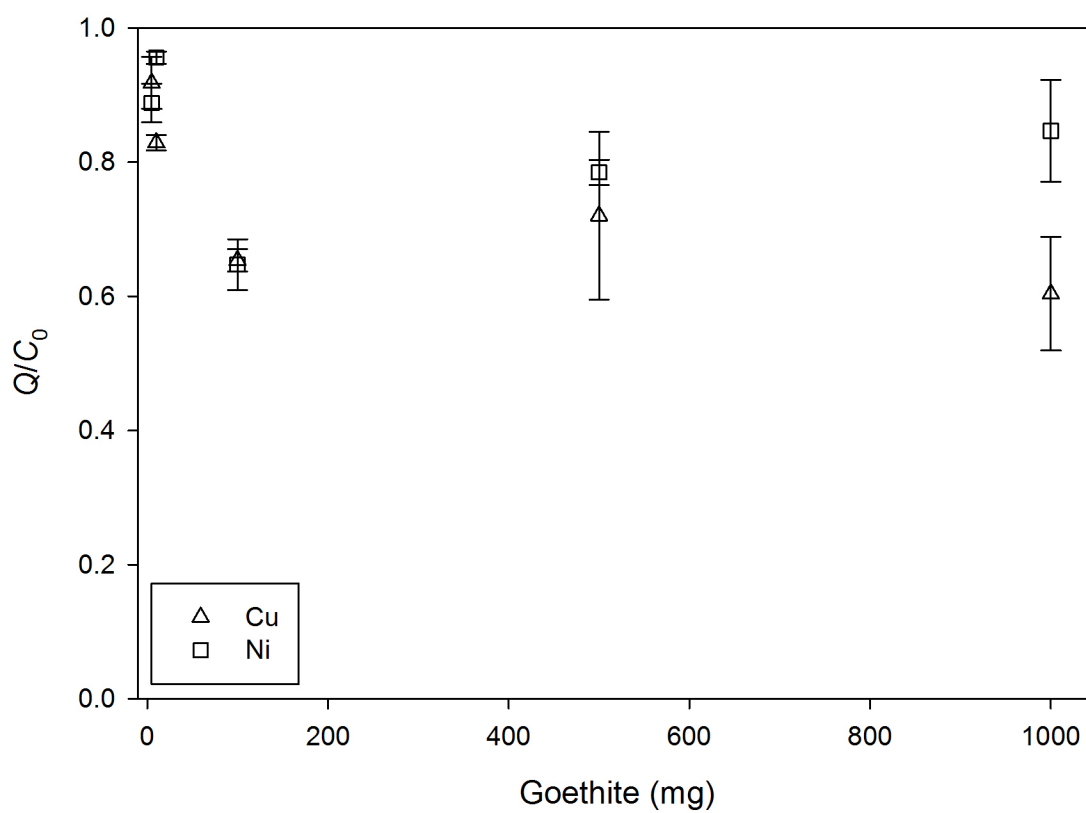
Figure A3. Solution amount ($C \pm 1$ SD) of Cu and Ni as a function of final pH (4–10) at constant goethite mass (5 mg), solute concentration (1000 nM Ni, 10000 nM Cu), and ionic strength (1 mM).
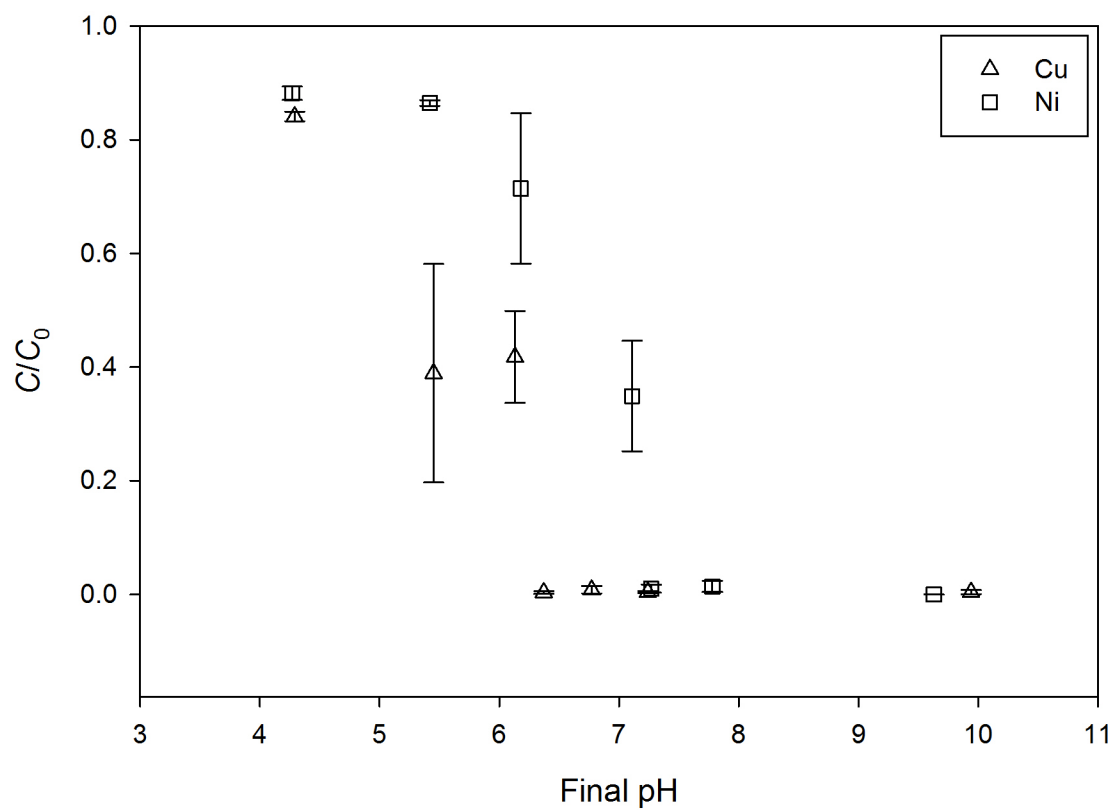
Figure A4. Adsorbed amount ($Q \pm 1$ SD) of Cu and Ni as a function of final pH (4–10) at constant goethite mass (5 mg), solute concentration (1000 nM Ni, 10000 nM Cu), and ionic strength (1 mM).