

Environmental Chemistry

COPPER AND NICKEL PARTITIONING WITH NANOSCALE GOETHITE
UNDER VARIABLE AQUATIC CONDITIONSKELSEY M. DANNER,[†] CHAD R. HAMMERSCHMIDT,*[†] DAVID M. COSTELLO,[‡] and G. ALLEN BURTON JR.[§][†]Department of Earth and Environmental Sciences, Wright State University, Dayton, Ohio, USA[‡]Department of Biological Sciences, Kent State University, Kent, Ohio, USA[§]School of Natural Resources and Environment, University of Michigan, Ann Arbor, Michigan, USA

(Submitted 16 October 2014; Returned for Revision 31 January 2015; Accepted 5 March 2015)

Abstract: Metal contaminated sediments can be toxic to aquatic organisms and are common in human-dominated ecosystems, which results in metals being a leading cause of ecosystem impairment. Bioavailability of metals is influenced by their affinity for dissolved and solid-phase ligands, including iron (Fe) oxyhydroxides, which have been hypothesized to reduce metal toxicity in sediments. The authors examined the adsorption kinetics of copper (Cu) and nickel (Ni) with goethite (α -FeOOH) and characterized the influences of solute metal concentration, pH, ionic strength, and humate concentration on steady-state partitioning of the metals with goethite under conditions representative of natural aquatic environments. Copper and Ni readily adsorbed to goethite, and steady-state partitioning was achieved within 2 h. Although ionic strength had no effect on metal partitioning, adsorption of Cu and Ni to goethite was enhanced by alkaline pH and reduced by competition with humate. Because distribution coefficient (K_D) values for Cu and Ni from the present study are comparable to values measured in natural systems, the authors hypothesize that goethite may contribute significantly to the adsorption of both Ni and Cu to particles in the environment. The authors suggest that incorporating binding by Fe oxides in metal bioavailability models should be a priority for improving risk assessment of metal-contaminated oxic sediments. *Environ Toxicol Chem* 2015;34:1705–1710. © 2015 SETAC

Keywords: Sediment chemistry Metal bioavailability Adsorption

INTRODUCTION

Metal contamination of sediments is a leading cause of ecosystem impairment as a result of metal toxicity to aquatic organisms [1,2]. Availability of metals (e.g., copper [Cu], nickel [Ni], zinc [Zn]) to organisms in sediments and the water column is influenced by their affinity for solid-phase sulfides, organic carbon, and metal oxides [3–8], as well as speciation with dissolved organic and inorganic ligands [9,10]. The current procedure used by the US Environmental Protection Agency (USEPA) for estimating metal bioavailability and toxicity in sediments is the equilibrium partitioning model [11]. The metal equilibrium partitioning model approach includes acidifying sediments and determining consequent concentrations of acid-volatile sulfide and simultaneously extracted metal. Sulfide complexes attenuate the toxicity of many metals in sediments [12]; however, whereas the equilibrium partitioning model approach is useful for predicting nontoxic thresholds for metals under reducing conditions in sediments, uncertainty exists in the method due to unaccounted metal binding by organic ligands and metal oxides.

Metals readily adsorb to iron (Fe) oxyhydroxides [13–17], which have been hypothesized to reduce metal bioavailability and toxicity in sediments [8,18]. Goethite (α -FeOOH) is the most abundant Fe oxyhydroxide in sediments [19,20] and known to complex divalent metals [14,15,17,21], mostly with hydroxyl functional groups [22,23]. Small diameter Fe oxyhydroxide particles, such as natural goethite (surface area = 45–

169 m² g⁻¹) [24], can have a significant concentration of hydroxyl surface ligands. Most of these ligands are protonated when the pH of surrounding water is less than the point of zero net proton charge, which is between approximately 5.9 and 6.7 for goethite [19]. When pH is greater than the point of zero net proton charge, however, iron oxyhydroxides have net negative surface charge and a greater abundance of unprotonated hydroxyl ligands to complex metals.

We experimentally investigated the steady-state partitioning of Cu and Ni between water and nanoscale goethite by varying the chemical composition of test solutions to encompass a wide range of conditions that occur in natural aquatic systems. In the present study, we were interested in examining the adsorption kinetics of Cu and Ni with goethite, as well as effects of the following factors on steady-state partitioning of Cu and Ni with goethite: 1) solute metal concentration, 2) pH, 3) ionic strength, and 4) humate concentration, which is an abundant and environmentally significant (competitive) ligand in natural waters [25,26]. The goal of the present study was to ascertain whether goethite may be an environmentally relevant sorbent for Cu and Ni in natural systems and thereby potentially attenuate metal toxicity.

MATERIALS AND METHODS

Reagents

Nanoscale goethite rods (0.05–0.15 μ m diameter, 0.4–1 μ m length; Nanostructured & Amorphous Materials) were cleaned prior to use by immersing in reagent-grade water (resistivity >18.2 M Ω -cm, pH = 7), shaking for 12 h at 150 rpm, decanting the water, and drying at 60 °C for 24 h. Heating goethite at 60 °C does not affect either its structure or composition [27,28]. The size of the goethite particles is representative of those in natural soils [29] and was selected to be large enough to be separated

All Supplemental Data may be found in the online version of this article.

* Address correspondence to chad.hammerschmidt@wright.edu

Published online 11 March 2015 in Wiley Online Library
(wileyonlinelibrary.com).

DOI: 10.1002/etc.2977

from water by membrane filtration. Cleaned goethite was analyzed for Ni and Cu so as to later differentiate the amount of either metal adsorbed during partitioning tests from that which is native to the mineral matrix as a trace contaminant. Stock solutions of Ni and Cu for partitioning tests were prepared by dissolving their dichloro salts (ACS grade) in reagent-grade water and titrating pH to neutrality with NaOH. Reagent-grade water was used as the solvent for all experiments, and ionic strength of experimental solutions was manipulated by adding either dissolved KCl or CaCl₂. Solution pH was adjusted with either dilute HCl (J.T. Baker Instra-Analyzed) or NaOH (ACS grade). Sodium humate (Aldrich) was used for competitive ligand tests with goethite. All reagents added negligible amounts of Cu and Ni to experimental solutions.

Experimental reactions

Partitioning of Cu and Ni with goethite was investigated under a variety of experimental conditions by reacting dissolved metals in 10 mL of water with a known mass of goethite in 15 mL polypropylene centrifuge tubes. Goethite was weighed (± 0.01 mg) into each tube so that known masses could be used to calculate distribution coefficients (K_D ; L kg⁻¹). Unless noted otherwise, all tests were conducted at ionic strength = 1 mM, which is typical of most fresh waters [30]. Moreover, but with the exception of tests with manipulated pH, the initial pH of all experimental solutions was circumneutral (~ 6 – 8). Four replicate tubes were prepared for each experimental treatment: 3 for analysis of either Cu or Ni in filtered water and adsorbed to goethite and 1 tube for determining initial and final pH. The pH electrode was calibrated before each use with buffers traceable to the US National Institute of Standards and Technology. Each reaction tube had a total solution volume of 10 mL, which included reagent-grade water, metal standard, KCl or CaCl₂ (to adjust ionic strength), and in some cases, dilute HCl, NaOH, and humate. Samples were allowed to react for a prescribed time on a rotary shaker table (150 rpm) at 25.0 ± 0.1 °C.

Reactions were terminated by separating the filter-passing aqueous phase from particulate goethite. After the reaction period, tubes were centrifuged at 2500 rpm for 10 min. Supernatant was decanted from the goethite pellet into 12-mL syringes equipped with luer-lock polycarbonate syringe filter holders (25 mm; Sartorius), encasing either hydrophilic polycarbonate membranes (0.01 μ m pore diameter) or polyether-sulfone membranes (0.03 μ m; Sterlitech Corporation), and filtered into a different tube. Nominal pore diameters of both filter types were sufficiently small to retain and separate nanoscale goethite (>0.05 μ m diameter, >0.4 μ m length) from the filtrate. All filtration equipment and sample tubes were cleaned with HCl and rinsed with reagent-grade water before use. After centrifugation and filtration, the goethite pellet and particles retained on the membrane filter were dissolved in 10 mL of 1 N HNO₃ (J. T. Baker Instra-Analyzed) and analyzed for adsorbed Cu and Ni, whereas the filtrate was acidified to 2% with HNO₃ and analyzed for Cu and Ni in solution.

Determination of nickel and copper

Nickel and Cu in acid-dissolved goethite (i.e., adsorbed) and filtered water (solute) were determined by inductively coupled plasma mass spectrometry with a PerkinElmer Elan 9000. Sample metal concentrations were measured after calibration with standard solutions traceable to the US National Institute of Standards and Technology. Quality control analyses included replicate samples and procedural blanks containing the full suite of reagents and taken through the reaction, filtration, and

extraction processes. Limits of quantification [30] were less than sample concentrations. Distribution coefficients (L kg⁻¹) of Cu and Ni between water and goethite were calculated by dividing the concentration of metal sorbed to goethite (mol kg⁻¹) by the solute metal concentration after reaction (mol L⁻¹).

Iron in filtered water

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 filtration membranes. Total Fe in samples and procedural standards was determined spectrophotometrically with a phenanthroline method (Standard Method 3500-Fe D) [30]. No colloidal and dissolved iron was detected in filtrates. The method detection limit of Fe analysis (8 μ M) was approximately 1000-fold less than the concentration of goethite in reaction tubes before filtration (5 mg goethite per 10 mL or ~ 6000 μ M).

RESULTS AND DISCUSSION

Sorbent mass

Adsorption of Ni and Cu to goethite was initially investigated by reacting a constant initial concentration of solute Ni (1000 nM) and Cu (10 000 nM) with varying masses of sorbent (5–1000 mg per 10 mL solution volume) for 24 h. More than 98% of added metal adsorbed to goethite among all sorbent mass treatments, illustrating the strong affinity of both metals for goethite (Supplemental Data, Figure S1). Because sorption of Cu and Ni to goethite appeared to be independent of sorbent mass within a range of 5 mg to 1000 mg at pH greater than the point of zero net proton charge, all future tests were conducted with only 5 mg to simplify goethite digestate matrixes and minimize pH buffering effects of goethite.

Adsorption kinetics

Copper and Ni adsorbed rapidly to goethite, and steady-state partitioning was achieved within 2 h (Supplemental Data, Figure S2). Adsorption of Cu and Ni to goethite was examined with reaction periods ranging from 2 h to 20 d. Distribution coefficients for the 500-nM and 5000-nM Ni treatments were within the same order of magnitude throughout the 20-d period, with K_D values in the 500-nM treatment increasing slightly with time (Pearson, $p = 0.01$; slope = $0.015 \log K_D$ d⁻¹) and those for the 5000-nM treatment remaining unchanged over time ($p = 0.5$). Distribution coefficients for the 5000-nM Cu treatment also were unchanged over time ($p = 0.6$), suggesting that a steady-state condition was maintained for at least 20 d.

We attempted to better resolve the adsorption kinetics of Ni to goethite by terminating partitioning reactions after 0.3 min, 2 min, 5 min, 10 min, 15 min, 30 min, and 120 min, followed immediately by a 10-min centrifugation period and filtration. Distribution coefficients for Ni after 0.3 min of reaction were comparable to those at the other time periods within the first 2 h (Supplemental Data, Figure S3). This suggests that adsorption of Ni to goethite was nearly instantaneous, and steady-state partitioning may be achieved more quickly than in 2 h, as noted above. Accordingly, results from all other tests, which were conducted for 24 h, are presumed to be representative of steady-state conditions.

Metal solute concentration

Solute concentration isotherms were prepared to estimate adsorption loading of goethite (5 mg) for Cu and Ni. Metal

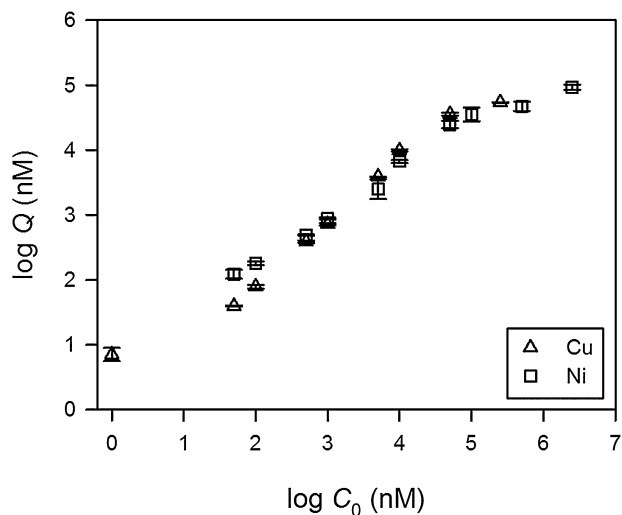


Figure 1. Amount of Cu and Ni adsorbed to goethite ($Q \pm 1$ standard deviation) as a function of initial solute metal concentration (C_0 ; 1 nM–2.5 μ M) at constant goethite mass (5 mg), pH = 7–9, and ionic strength = 1 mM.

concentrations used for these tests ranged from 50 nM to 2.5×10^6 nM of Ni and from 1 nM to 2.5×10^5 nM of Cu. Metal concentrations at the lower end of the test ranges are representative of those found in natural and contaminated waters [31,32], whereas those at the high end exceed typical concentrations in the environment. Nonetheless, the amount of Cu and Ni adsorbed to goethite increased with initial solute concentration (Figure 1), even at environmentally unrealistic metal concentrations, indicating that goethite has a high capacity for metal adsorption.

We estimated the adsorption loading of nanoscale goethite for Cu and Ni at the maximum test concentrations. Adsorption loading (atoms nm^{-2}) of nanoscale goethite was determined from adsorbed amounts of Ni and Cu according to the following equation:

$$\text{Adsorption loading} = (Me/M) \times SSA \times N \quad (1)$$

where, Me is the amount of metal (mol) adsorbed to goethite, M is the mass of goethite sorbent (g), SSA is the specific surface area of goethite ($4\text{--}6 \times 10^{19} \text{ nm}^2 \text{ g}^{-1}$; Nanostructured & Amorphous Materials), and N is Avogadro's number. The adsorption loading of goethite with 2.5×10^5 nM Cu ranged from 1.1 Cu atoms nm^{-2} to 1.9 Cu atoms nm^{-2} . Adsorption loading of goethite with 2.5×10^6 nM Ni ranged from 1.7 Ni atoms nm^{-2} to 3.3 Ni atoms nm^{-2} . Such loadings are close to the lower range of surface-site densities on goethite ($2.6\text{--}16.8 \text{ nm}^{-2}$) [33], which is the maximum number of binding sites available for metal complexation. The range of adsorption loadings for nanoscale goethite estimated from the present study is in good agreement with an adsorption loading of 1.1 Cu atoms nm^{-2} determined for micron-scale goethite with $\geq 5 \times 10^5$ nM Cu [15].

pH

Steady-state partitioning of Cu and Ni with goethite varied markedly as a function of pH (Figure 2). Partitioning tests were conducted with solution pH values ranging from 4 to 10, which bracket the point of zero net proton charge of goethite (5.9–6.7) [19]. Distribution coefficients of Cu and Ni were approximately 10^2 L kg^{-1} at pH 4.3 and increased exponentially along adsorption edges to an asymptotic value

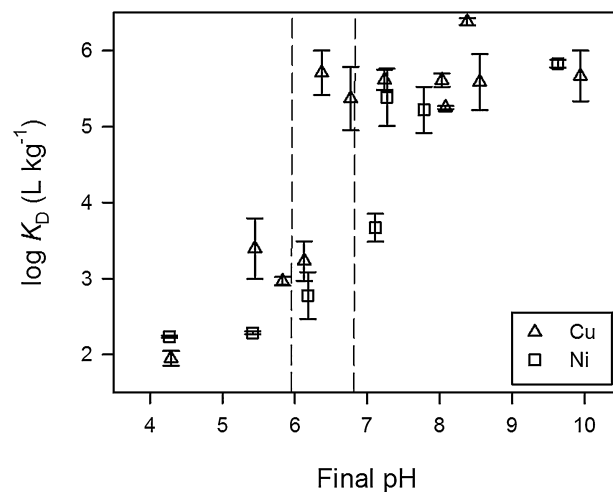


Figure 2. Distribution coefficients ($K_D \pm 1$ standard deviation) of Cu and Ni as a function of pH with a constant goethite mass (5 mg), initial solute metal concentration (1000 nM Ni, 10 000 nM Cu) and ionic strength (1 mM). Dashed lines indicate the range of the point of zero net proton charge of goethite according to Langmuir [19].

of approximately $10^{5.5} \text{ L kg}^{-1}$ when pH was greater than approximately 7.3 (relationships between pH 4.3 and 7.3: $\log K_{D, \text{Ni}} = 0.877 \times \text{pH} - 1.997$, $r^2 = 0.68$; $\log K_{D, \text{Cu}} = 1.37 \times \text{pH} - 4.210$, $r^2 = 0.77$). Relationships between the K_D values and pH are consistent with goethite having decreased availability of surface ligands when the pH is less than the point of zero net proton charge and greater ligand activity at higher pH. Greater metal adsorption to goethite at alkaline pH also may be attributed to relatively more of the Cu and Ni existing as the CuOH^+ and NiOH^+ species, which are the ion pairs hypothesized to preferentially sorb to Fe oxides [34].

Ionic strength

Ionic strengths ranging from those of rainwater (0.02 mM) to that in excess of seawater (1000 mM) had no effect on the partitioning of either Ni or Cu to goethite (Supplemental Data, Figure S4). Distribution coefficients of both metals were unrelated to ionic strength when K^+ and Cl^- were the major ions in solution (Spearman, p values >0.3). Moreover, the partitioning of Cu to goethite was not different, whether either KCl or CaCl_2 were used to adjust ionic strength to either 0.1 mM or 250 mM (Mann–Whitney rank sum, p values >0.05). It was anticipated that increasing ionic strength, as well as the chloride concentration, might decrease adsorption of Ni and Cu by goethite due to competitive complexation of the metals by chloride; however, chloride concentration had no effect on partitioning of either Cu or Ni. Similar to the present study, Ni adsorption to amorphous $\text{Fe}(\text{OH})_3$ [35] and cadmium adsorption to goethite were unaffected by ionic strength [36]. Independence of Cu and Ni partitioning as a function of ionic strength is consistent with both metals associating dominantly with goethite surface ligands, which appear to be affected insignificantly by ionic strength, as opposed to surface charge attraction.

Humate

Adding humate as a competitive ligand for complexing Cu and Ni in solution decreased adsorption of the metals to goethite (Figure 3) as expected. A relatively 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

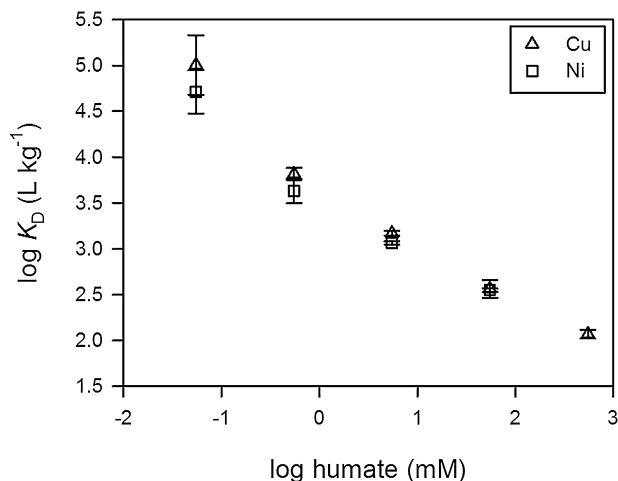


Figure 3. Distribution coefficients ($K_D \pm 1$ standard deviation) of Cu and Ni as a function of nominal humate concentration (0.055–550 mM) at constant goethite mass (5 mg), initial solute metal concentration (1000 nM Ni, 10 000 nM Cu), pH = 7–10, and ionic strength = 1 mM.

rank sum, p values >0.7). A 0.055 mM concentration of humate corresponds to a dissolved organic carbon (DOC) concentration of approximately 5 mM, assuming Aldrich humate contains approximately 70% carbon by weight [37] and has a molecular weight of 1630 g mol⁻¹ [38], which is either comparable to or greater than DOC concentrations in most natural surface waters (0.1–0.7 mM) [39] and sediment pore fluids (1–13 mM) [40]. Concentrations of humate greater than 0.055 mM resulted in a decrease of the K_D . These results are consistent with the known affinities of Ni (log K' = 3–6 at pH = 7 and ionic strength = 200 mM) [41] and Cu (log K' = 5 at pH = 3.5) [42] for humate, which by complexing metals can reduce toxicity to aquatic invertebrates [43]. Moreover, these results illustrate that, at relatively high concentrations, dissolved organic ligands can attenuate the potential significance of goethite for binding Cu and Ni. Humate additions proportionately increased solution pH (maximum pH = 10 in the 55 mM humate treatment), which enhances metal binding to goethite (Figure 2), but the increase of pH did not increase adsorption of Cu and Ni to goethite in the presence of humate.

The mechanism by which humate attenuated adsorption of Cu and Ni to goethite is likely by complexing the metals and keeping them in solution. Organic ligands can themselves adsorb to metal oxide surfaces and affect apparent metal partitioning by either complexing metals in a goethite–humate–metal ternary complex or by physically blocking surface sites of the metal oxide [44–47]. The observed decrease in metal adsorption to goethite with increasing humate and pH is inconsistent with either goethite–metal–humate ternary complexation or humate-blocking surface sites on goethite as being important because humate adsorption to goethite decreases with increasing pH [48].

Environmental implications

The environmentally realistic conditions mimicked in the present study resulted in distribution coefficients for Ni and Cu with goethite that are comparable to, if not greater than, summary values reported for natural freshwater/particle interfaces in the United States. Median log K_D values are 4.0 L kg⁻¹ for Ni and 4.2 L kg⁻¹ for Cu partitioning between sediment and water [49]. Log K_D values for Cu and Ni with

goethite ranged from 3.5 to 5 under laboratory conditions that were most representative of conditions in natural sediments: pH = 6 to 8, ionic strength = 1 mM [30], DOC = 1 mM to 13 mM [40], and concentrations of filtered Ni = 10 nM to 1000 nM [50] and Cu = 3 nM to 450 nM [31]. Because K_D values from the present study are comparable to those in natural systems, we hypothesize that goethite may contribute significantly to the adsorption of both Ni and Cu onto sediments that are composed of a variety of ligands.

The present study suggests that Ni and Cu adsorption to goethite in natural systems is controlled largely by porewater pH and competition from other ligands. Therefore, metal adsorption to goethite will be most prevalent in aquatic environments having circumneutral to alkaline pH with relatively low concentrations of organic ligands and reduced sulfur. Surficial sediments, which are characterized by oxygenated porewaters, rapid respiration of organic carbon, and low concentrations of reduced sulfur [51], are a likely location for goethite to be a significant ligand. Formation of goethite and potentially other Fe and Mn oxyhydroxides in both surface sediments and the water column may effectively scavenge other metals from solution, including porewaters, and reduce their bioavailability, as observed in sediments incubated under natural stream flow conditions [8,18]. In environments having a pH less than neutral, sulfides and organic matter will likely be more significant solid-phase ligands than goethite for complexing Ni and Cu and, by extension, other divalent metals. Metal adsorption by goethite is highly pH-dependent, and natural changes of solution pH could result in variable metal solubility. In particular, metal-goethite associations would be expected to vary as a function of pH/Eh oscillations at the sediment–water interface [52]. Hence, and in addition to its effect on speciation of dissolved metals, low pH potentially exacerbates metal solubility and toxicity. This is a result of its influence on the complexing capacity of goethite and, by extension, other minerals with pH-dependent surface ligands and charges.

In addition to improving our understanding of metal biogeochemistry in sediments, these results provide important information for the risk assessment of metals in sediments. The association of metals with solid-phase ligands has long been recognized as important for attenuating the toxicity of metals to aquatic biota [53], and many studies have attempted to use models of metal speciation to better predict toxic thresholds [11,54]. The current models, which account for complexation by reduced sulfur and organic carbon, have well-known uncertainty in the thresholds where toxicity is expected [11,18,54], and some of that uncertainty may be because of unaccounted binding by Fe oxides. The measured K_D for Cu and Ni complexing with goethite approached the same magnitude for metals binding to organic matter (median organic carbon partition coefficient [$\log K_{OC}$] = 5.1 L kg⁻¹ and 5.5 L kg⁻¹ for Ni and Cu, respectively) [49]. This suggests that the role of Fe oxide may be as important as organic carbon under certain environmental conditions, particularly alkaline pH. More accurate estimates of metal bioavailability, therefore, will require including Fe oxides in the solid-phase ligand pool to avoid overestimating the concentration of bioavailable metal. Furthermore, measuring sediment pH would improve predictions of metal bound to organic carbon [54] and oxide surfaces and should be included in next-generation models of metal bioavailability. Collectively, characterizing basic sediment physicochemistry (e.g., pH, redox potential) and accounting for pools of important metal-binding ligands should allow for a more robust estimation of metal bioavailability.

SUPPLEMENTAL DATA

Figures S1–S4. (470 KB DOC).

Acknowledgment—The present study was supported by grants from the Nickel Producers Environmental Research Association, Rio Tinto, International Lead Zinc Research Organization, International Copper Association, Cobalt Development Institute, and Vanitec, as well as a Wright State Graduate Council Fellowship to K.M. Danner. We thank K. Alcorn, R. Gamby, D. Marsh, and B. Shields for laboratory assistance.

Disclaimer—The authors report no conflict of interest. The authors alone are responsible for the content and writing of the present study.

Data availability—All data, associated metadata, and calculation tools are available on request from the authors (chad.hammerschmidt@wright.edu).

REFERENCES

- Chapman PM, Wang F, Janssen C, Persoone G, Allen HE. 1998. Ecotoxicology of metals in aquatic sediments: Binding and release, bioavailability, risk assessment, and remediation. *Can J Fish Aquat Sci* 55:2221–2243.
- US Environmental Protection Agency. 2014. National summary of impaired waters and TMDL information. Washington, DC. [cited 2014 January 22]. Available from: http://iaspub.epa.gov/waters10/attains_nation_cy.control?p_report_type=T
- Lion LW, Altmann RS, Leckie JO. 1982. Trace-metal adsorption characteristics of estuarine particulate matter: Evaluation of contributions of Fe/Mn oxide and organic surface coatings. *Environ Sci Technol* 16:660–666.
- Dzombak DA, Morel, FMM. 1990. *Surface Complexation Modeling: Hydrous Ferric Oxide*. John Wiley & Sons, Hoboken, NJ, USA.
- Benoit G, Oktay-Marshall SD, Cantu II A, Hood EM, Coleman CH, Corapcioglu MO, Santschi PH. 1994. Partitioning of Cu, Pb, Ag, Zn, Fe, Al, and Mn between filter-retained particles, colloids, and solution in six Texas estuaries. *Mar Chem* 45:307–336.
- Hammerschmidt CR, Fitzgerald WF. 2004. Geochemical controls on the production and distribution of methylmercury in near-shore marine sediments. *Environ Sci Technol* 38:1487–1495.
- Jeong HY, Klaue B, Blum JD, Hayes KF. 2007. Sorption of mercuric ion by synthetic nanocrystalline mackinawite (FeS). *Environ Sci Technol* 41:7699–7705.
- Costello DM, Burton GA, Hammerschmidt CR, Taulbee WK. 2012. Evaluating the performance of diffusive gradients in thin films for predicting Ni sediment toxicity. *Environ Sci Technol* 46:10239–10246.
- Tessier A, Campbell PGC. 1987. Partitioning of trace metals in sediments: Relationships with bioavailability. *Hydrobiologia* 149:43–52.
- Allen HE, Hansen DJ. 1996. The importance of trace metal speciation to water quality criteria. *Water Environ Res* 68:42–54.
- US Environmental Protection Agency. 2005. Procedures for the derivation of equilibrium partitioning sediment benchmarks (ESBs) for the protection of benthic organisms: Metal mixtures (cadmium, copper, lead, nickel, silver and zinc). EPA/600/R/02/011. Office of Research and Development, Washington, DC.
- Morse JW, Luther GW III. 1999. Chemical influences on trace metal-sulfide interactions in anoxic sediments. *Geochim Cosmochim Acta* 63:3373–3378.
- Amacher MC, Kotuby-Amacher J, Selim HM, Iskandar IK. 1986. Retention and release of metals by soils—Evaluation of several models. *Geoderma* 38:131–154.
- Grossl PR, Sparks DL. 1994. Rapid kinetics of Cu(II) adsorption/desorption on goethite. *Environ Sci Technol* 28:1422–1429.
- Coughlin BR, Stone AT. 1995. Nonreversible adsorption of divalent metal ions (Mn^{II}, Co^{II}, Ni^{II}, Cu^{II}, and Pb^{II}) onto goethite: Effects of acidification, Fe^{II} addition, and picolinic acid addition. *Environ Sci Technol* 29:2445–2455.
- Ford RG, Bertsch PM, Farley KJ. 1997. Changes in transition and heavy metal partitioning during hydrous iron oxide aging. *Environ Sci Technol* 31:2028–2033.
- Trivedi P, Axe L. 2001. Ni and Zn sorption to amorphous versus crystalline iron oxides: Macroscopic studies. *J Colloid Interface Sci* 224:221–229.
- Costello DM, Burton GA, Hammerschmidt CR, Rogevich EC, Schlekot CE. 2011. Nickel phase partitioning and toxicity in field-deployed sediments. *Environ Sci Technol* 45:5798–5805.
- Langmuir D. 1997. *Aqueous Environmental Geochemistry*. Prentice Hall, Upper Saddle River, NJ, USA.
- van der Zee C, Roberts DR, Rancourt DG, Slomp CP. 2003. Nanogoethite is the dominant reactive oxyhydroxide phase in lake and marine sediments. *Geology* 31:993–996.
- Davis AP, Upadhyaya M. 1996. Desorption of cadmium from goethite-55e (α-FeOOH). *Water Res* 30:1894–1904.
- Parfitt RL, Russell JD, Farmer VC. 1976. Confirmation of the surface structures of goethite (α-FeOOH) and phosphated goethite by infrared spectroscopy. *J Chem Soc Faraday T 1* 72:1082–1087.
- Parfitt RL, Russell JD. 1977. Adsorption on hydrous oxides. IV. Mechanisms of adsorption of various ions on goethite. *J Soil Sci* 28:297–305.
- Catts JG. 1982. Adsorption of Cu, Pb, Zn onto birnessite. PhD thesis, Colorado School of Mines, Golden, CO, USA.
- Kinniburgh DG, Milne CJ, Benedetti MF, Pinheiro JP, Filius J, Koopal LK, Van Riensdijk WH. 1996. Metal ion binding by humic acid: Application of the NICA-Donnan model. *Environ Sci Technol* 30:1687–1698.
- Milne CJ, Kinniburgh DG, van Riensdijk WH, Tipping E. 2003. Generic NICA-Donnan model parameters for metal-ion binding by humic substances. *Environ Sci Technol* 37:958–971.
- Koch CJW, Madsen MB, Mørup S, Christiansen G, Gerward L, Villadsen J. 1986. Effect of heating on microcrystalline synthetic goethite. *Clays Clay Miner* 34:17–24.
- Waychunas GA, Kim CS, Banfield JF. 2005. Nanoparticulate iron oxide minerals in soils and sediments: Unique properties and contaminant scavenging mechanisms. *Journal of Nanoparticle Research* 7:409–433.
- Schwertmann U, Taylor RM. 1989. Iron oxides. In Dixon JB, Weed SB, eds, *Minerals in Soil Environments*. Soil Science Society of America, Madison, WI, USA, pp 379–438.
- American Public Health Association, American Water Works Association, and Water Environment Federation. 1995. *Standard Methods for the Examination of Water and Wastewater*, 19th ed. Washington, DC, USA.
- Bowen HJM. 1985. *The cycles of copper, silver and gold*. In Hutzinger D, ed, *The Natural Environment and the Biogeochemical Cycles*. Springer-Verlag, New York, NY, USA, pp 1–27.
- Agency for Toxic Substances and Disease Registry. 2005. *Toxicological Profile for Nickel*. US Department of Health and Human Services, Public Health Service, Washington, DC.
- Davis JA, Kent DB. 1990. Surface complexation modeling in aqueous geochemistry. In Hochella Jr. MF, White AF, eds, *Mineral-Water Interface Geochemistry*. Mineralogical Society of America, Washington, DC, USA, pp. 177–260.
- Rai D, Zachara A, Schwab R, Schmidt R, Girvin D, Rogers J. 1984. Chemical attenuation rates, coefficients, and constants in leachate migration. Vol. 1: A critical review. EPRI EA-3356. Final Report. Battelle Pacific Northwest Laboratories, Richland, WA, USA.
- Green-Pedersen H, Jensen BT, Pind N. 1997. Nickel adsorption on MnO₂, Fe(OH)₃, montmorillonite, humic acid and calcite: A comparative study. *Environ Technol* 18:807–815.
- Hayes KF, Leckie JO. 1987. Modeling ionic strength effects on cation adsorption at hydrous oxide/solution interfaces. *J Colloid Interface Sci* 115:564–572.
- Chiou CT, Kile DE, Brinton TI, Malcolm RL, Leenheer JA. 1987. A comparison of water solubility enhancements of organic solutes by aquatic humic materials and commercial humic acids. *Environ Sci Technol* 21:1231–1234.
- Chin YP, Aiken GR, Danielsen KM. 1997. Binding of pyrene to aquatic and commercial humic substances: The role of molecular weight and aromaticity. *Environ Sci Technol* 31:1630–1635.
- Spitz A, Leenheer J. 1991. Dissolved organic carbon in rivers. In Degens ET, Kempe S, Richey JE, eds, *SCOPE 42—Biogeochemistry of Major World Rivers*. Scientific Committee on Problems of the Environment, Paris, France.
- Orem WH, Lerch HE, Rawlik P. 1997. Geochemistry of surface and pore water at USGS coring sites in wetlands of South Florida, 1994–1995. OFR 97–454. US Geological Survey, Reston, VA.
- Glaus MA, Hummel W, Van Loon LR. 2000. Trace metal–humate interactions. I. Experimental determination of conditional stability constants. *Appl Geochem* 15:953–973.
- Pandey AK, Pandey SD, Misra V. 2000. Stability constants of metal-humic acid complexes and its role in environmental detoxification. *Ecotoxicol Environ Saf* 47:195–200.

43. Cloran CE, Burton GA, Hammerschmidt CR, Taulbee WK, Custer KW, Bowman KL. 2010. Effects of suspended solids and dissolved organic carbon on nickel toxicity. *Environ Toxicol Chem* 29:1781–1787.
44. Schwertmann U. 1991. Solubility and dissolution of iron oxides. *Plant Soil* 130:1–25.
45. Kim CS, Rytuba JJ, Brown, Jr., GE. 2004. EXAFS study of mercury(II) sorption to Fe- and Al-(hydr) oxides. II. Effects of chloride and sulfate. *J Colloid Interface Sci* 270:9–20.
46. Saito T, Koopal LK, Nagasaki S, Tanaka S. 2005. Analysis of copper binding in the ternary system Cu^{2+} /humic acid/goethite at neutral to acidic pH. *Environ Sci Technol* 39:4886–4893.
47. Reiller P, Amekraz B, Moulin C. 2006. Sorption of Aldrich humic acid onto hematite: Insights into fractionation phenomena by electrospray ionization with quadrupole time-of-flight mass spectrometry. *Environ Sci Technol* 40:2235–2241.
48. Reiller P, Moulin V, Casanova F, Dautel C. 2002. Retention behaviour of humic substances onto mineral surfaces and consequences upon thorium (IV) mobility: Case of iron oxides. *Appl. Geochem. Appl Geochem* 17:1551–1562.
49. Allison, JD, Allison TL. 2005. Partition coefficients for metals in surface water, soil, and waste. EPA 600/R-05/074. US Environmental Protection, Washington, DC.
50. Sutherland JE, Costa M. 2002. Nickel. In Sarkar B, ed, *Heavy Metals in the Environment*. Dekker, New York, NY, USA, pp 349–408.
51. Boudreau BP, Jørgensen BB. 2001. *The Benthic Boundary Layer: Transport Processes and Biogeochemistry*. Oxford University Press, New York, NY, USA.
52. Nimick DA, Gammons CH, Cleasby TE, Madison JP, Skaar D, Brick CM. 2003. Diel cycles in dissolved metal concentrations in streams: Occurrence and possible causes. *Water Resour Res* 39:1247–1256.
53. Ankley GT, Di Toro DM, Hansen DJ, Berry WJ. 2009. Technical basis and proposal for deriving sediment quality criteria for metals. *Environ Toxicol Chem* 15:2056–2066.
54. Di Toro DM, McGrath JA, Hansen DJ, Berry WJ, Paquin PR, Mathew R, Wu KB, Santore RC. 2005. Predicting sediment metal toxicity using a sediment biotic ligand model: Methodology and application. *Environ Toxicol Chem* 24:2410–2427.